GEOCHIMICA ET COSMOCHIMICA ACTA

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VOLUME 10, NOS. 5/6 NOVEMBER 1956

CONTENTS

PAGE

KARL K. TUREKIAN and J. LAURENCE KULP: The geochemistry of strontium . . . 245

A. E. RINGWOOD: Melting relationships of Ni-Mg olivines and some geochemical implications 297

PER GEIJER: Pre-Cambrian atmosphere: evidence from the Pre-Cambrian of Sweden . 304

A. J. MAJUMDAR and RUSTUM ROY: Fugacities and free energies of CO_2 at high pressures and temperatures 311

GEORGE T. FAUST, K. J. MURATA, and JOSEPH J. FAHEY: Relation of minor-element content of serpentines to their geological origin 316

Geochemical Notes:

SAYED A. WARDANI: Germanium in meteorites 321

D. F. C. MORRIS: The association of nickel with cinnabar 322

Book Review:

"Cosmologie et Chimie" by ALEXANDRE DAUVILLIER (reviewed by F. A. PANETH) . 324

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The geochemistry of strontium*

KARL K. TUREKIAN† and J. LAURENCE KULP
Lamont Geological Observatory (Columbia University) Palisades, New York

(*Received* 6 *March* 1956, *in revised form* 10 *April* 1956)

Abstract—The geochemistry of strontium has been investigated, using an emission spectrographic technique checked by isotope dilution analyses described elsewhere (TUREKIAN *et al.*, in press). Hence the determinations are claimed to have good accuracy as well as precision.

Approximately 700 analyses have been made on silicate rocks and over 300 on carbonate materials (a detailed analysis of the latter appearing in other papers). An attempt was made at a representative sampling of the crust of the earth.

The difference in behaviour of strontium relative to calcium in granitic rocks as compared to basaltic rocks is striking. For granitic rocks there is an increase of strontium content with an increase in calcium not only for samples from a single batholith but also when extended to a universal sampling. On the other hand, though some differentiated basaltic bodies show a covariance of strontium and calcium, it is always with the strontium content increasing as the calcium content decreases. On a worldwide basis, however, this relationship is destroyed because marked regional variations subdue any differentiation effects that might be present locally.

The crustal abundance of strontium in basaltic rocks may be estimated without difficulty by taking a simple average, but a similar procedure for granitic rocks is ruled out because of the dependence of strontium content on rock-type. The table below summarizes the abundances of strontium in the various phases of the earth's crust.

Abundance of strontium in the crust

Rock	Avg. % calcium	Avg. p.p.m. strontium	$\frac{\%Sr}{\%Ca} \times 10^3$
Basaltic rocks (245)	7·1	465	6·5
Granitic rocks (175)			
0·1–1·0% Ca	0·6	100	16·7
1·0–5·0% Ca	1·9	440	23·0
Sedimentary rocks			
Limestone (150)	40·0	610	1·5
"Average" shale (69)	5·0	300	6·0
Calcareous deep-sea sediments	35·0	2075	5·9
Sea (ODUM)	—	—	20·2
Cosmic (SUESS and UREY, 1956)	—	—	0·84

If it is assumed that the crust is mainly basaltic and granodioritic, the crustal abundance of strontium would be 450 p.p.m. Applications of the data to petrogenetic problems, sedimentary cycles, and the evolutionary development of marine invertebrates are discussed.

INTRODUCTION

ONE of the tasks of geochemistry is to evaluate accurately the abundance and pattern of distribution of the elements in the earth. Such information contributes to the solution of a wide variety of geologic problems.

The possibility that the previously accepted abundance for strontium

* Lamont Geological Observatory Contribution No. 201

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(150 p.p.m., Goldschmidt, 1954) is incorrect was pointed up by an anomaly in the isotope geology of the element. Wickman (1948), using available estimates of strontium and rubidium for the crust of the earth, calculated a 6% increase in Sr^{87}/Sr^{86} ratio per billion years in limestones, whereas Gast (1955) actually found less than 0·4% increase per billion years. This discrepancy is well outside the experimental error and emphasizes the uncertainty not only in the abundances of Rb and Sr but possibly in the geochemistry of strontium as well.

The three factors, i.e. extent of sampling, selective sampling, and analytical errors, which cause the uncertainty in the older values, have been studied in an effort to control them.

First, a large number of geologic materials have been investigated. A total of some 1000 analyses have been completed. Second, an attempt was made to sample the earth in as representative a manner as possible. Needless to say, the result is still somewhat unsatisfactory, but is a considerable improvement over earlier efforts. Third, the convenient and rapid technique of emission spectrography was subjected to absolute calibration by using isotope dilution technique in analysing standard samples. The analytical technique used is described elsewhere (Turekian *et al.*, 1956, in press).

In addition to determining the absolute abundance of strontium and evaluating the pattern of distribution, this study yields information on certain problems of petrogenesis, palaeoecology, and geochemical cycles. This investigation points up the desirability of re-examining the geochemistry of other trace elements with modern techniques.

Historical Survey

There have been only two attempts to evaluate the role of strontium in the crust of the earth. Noll (1934), working under Goldschmidt, established many of the principles of strontium distribution. Though he made a survey of the reliability of the wet-chemical methods used in earlier analyses and concluded that only one method could give even fair results, yet in estimating the crustal abundance of strontium he used all of the published data uncritically and obtained a value for the crust of 150 p.p.m. Noll's main contribution was to utilize effectively the new tool of X-ray fluorescence for the quantitative analysis of minerals for strontium. Hevesy and Würstlin (1934), also using the X-ray fluorescence technique, analysed a limited number of silicates for strontium.

Odum (1950, 1951a, 1951b) did his main work on the biogeochemistry of strontium. Most of his determinations were on biological and related materials, and include the first acceptable analyses of strontium in sea-water and in the tests of living and fossil organisms. His analyses, made with a modified flame photometer, are in good agreement with comparable samples analysed in the present work.

There are other analyses of strontium in rocks and minerals scattered through the literature. Most of these analyses, however, relate to peculiar rock suites, and the level of accuracy is not claimed to be high. Usually the analysis has been part of a general scheme of investigation for a large number of trace elements. As it has been shown that wide variations are possible among investigators for strontium analyses, it is best to exclude all of these reports until it can be established which are good enough to be included in an accurate estimate of crustal abundance.

Results

The results of analyses on the silicate rocks and minerals are found mainly in Tables 1–4. Additional data are found throughout the text as the particular information is related to the discussion. The analyses are reported as per cent

Table 1. Basaltic rocks

Number	Description	Percentage Ca	p.p.m. Sr
	I. Oceanic Islands		
A. Pacific			
1. *Hawaii*			
AD 22	Basalt, top of Mauna Loa	6·6	257
AD 23	Olivine basalt, Mauna Loa	7·5	280
AD 24	Basalt, falls near Hilo	6·4	422
AD 25	Olivine-rich basalt, crater of Kilauea	6·2	429
AD 26	Basalt, nr. Lahaina, Maui	7·5	404
AD 27	Basalt, summit of Mt. Haleakala, Maui	5·8	1367
AD 28	Basalt, olivine free (Koolau series), Kaukonahua Gulch, Oahu	6·4	348
AD 29	Olivine basalt, Kaena Pt., Oahu	6·0	846
AD 30	Olivine basalt, Kolua, Kauaii	4·7	232
SD 1	Ol. basalt, prehistoric flow from Mauna Loa	8·9	347
SD 2	Ol. basalt, prehistoric flow from Kilauea	7·7	392
SD 3	Andesine andesite, nr. Nohonaohae cave, Mauna Kea	6·3	1200
SD 4	Melilite-nepheline basalt, Manuhonohono cave, Kauai	9·9	1230
SD 5	Ol. basalt, prehistoric flow from Mauna Loa	7·2	430
SD 6	Oligoclase andesite, Kohala Mt.	4·2	1048
SD 7	1950 lava of Mauna Loa	7·2	349
SD 9	Oligoclase gabbro (Kauaiite), Kauai	7·6	963
SD 10	Basalt w. feldspar phenocrysts, Kohala Mt.	6·9	610
SD 11	Picritic basalt, ankaramite type, Mauna Kea	7·6	365
SD 12	Nepheline basalt, Kauai	9·1	984
SD 13	Trachyte obsidian, Hualalai	0·61	43
SD 14	Picritic basalt (oceanite), 1852 flow, Mauna Loa	5·8	297
SD 15	Olivine gabbro porphyry, Uwekahuna laccolith, Kilauea caldera	5·3	267
2. *Other Intra-Pacific Islands*			
AD 31	Lava, Galapagos	6·9	262
AD 32	Scoria, Tahiti	7·5	247
AD 33	Basalt, Tutuila, Samoa	6·7	495
AD 34	Basalt ankaramitique, Tahiti	7·4	1060
AD 35	Basalt, NW side Vita Levu, Fiji	9·5	935
RD 1	Basalt labr. (β), Oua-Pou, Marquises	8·4	696
RD 2	Basalt labr. (β), Vanikoro	8·2	289
RD 3	Basalt labr. (α), Ambrym eruption of 1913	7·2	558
RD 4	Basalt labr. (β), Mangareva	8·6	331
RD 5	Basalt labr (α), Mangareva	9·1	295
RD 6	Basalt andés. (α), Maupiti	6·2	629
RD 7	Basalt labr. (β), Hoane, Ma-Muka, Marquises	6·7	681
RD 8	Basalt doléritique, Vaipae, Ma-Muka, Marquises	6·4	785
RD 9	Basalt labr. (β), Hikeu, Ma-Pou, Marquises	7·4	735
RD 10	Basalt andés. (β), Tahoa	6·7	705
RD 12	Basalt labr. (β), Gambies, Mangareva	9·2	379
RD 13	Basalt labr. (β), Gambies, Mangareva	7·5	409

Table 1 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
2. *Other Intra-Pacific Islands* (*continued*)			
RD 14	Basalt labr. (β), Nuku-Hiva, Marquises	6·7	505
RD 15	Basalt labr. (β), Ancytaim, Nlles Hebrides	9·5	376
RD 16	Basalt labr. (β), Toopua, Bora-Bora	7·1	849
RD 17	Basalt ankaram., Ma-Huka, Hoane	8·5	412
3. *Japan and Aleutians*			
AD 2	Ol. basalt, Noto Peninsula, Ishikawa, Japan	6·9	980
AD 11	Non-prophyritic basalt, Shimotanna, Izu, Japan	7·4	241
AD 12	Pigeonite andesite, Hakone caldera, Shizuoka, Japan	8·1	202
AD 13	Pyroxene ol. basalt, Shimotanna, Izu, Japan	5·9	247
KD 1	Ol. basalt (Holocene), S. of Saigo, Dogo, Oki I, Japan	8·2	579
KD 3	Aphyric basalt (Pliocene?) Okata, Osima I., Izu, Japan	8·4	145
KD 4	Ol. trachybasalt (Pleistocene?) Gembrudo, nr. Kyoto, Japan	5·8	710
KD 8	Ol. andesite (Miocene), N of Kamitugu, Aiti, Japan	5·6	278
KD 10	Dolerite (Miocene) nr. Semi, Yamagata, Japan	6·4	222
UD 1	Basalt, (Pleistocene or Recent) Unalaska I., Aleutians	7·3	615
UD 2	Basalt (Pliocene (?) or Pleistocene) Unalaska I., Aleutians	5·8	224
UD 3	Basalt Miocene (?), Ballyhoo Mt., Unalaska I., Aleutians	5·6	352
B. Atlantic and Indian Oceans			
AD 36	Ol. basalt, Jamestown, St. Helena	9·6	710
AD 37	Ol. basalt, Funchal, Madeira	10·5	650
AD 38	Ol. basalt, Ile de France, Mauritius	9·2	472
AD 39	Ol. basalt, Horta, Fayal, Azores	8·6	1090
II. EUROPEAN SUITES			
A. Switzerland—Spilites			
ID 1	"Variolite", Hörnli near Arosa, Graubünden	4·0	94
ID 2	"intersertal", Hörnli near Arosa, Graubünden	4·1	220
ID 3	"intersertal", Hauen-Jaunpass, Bern	0·78	51
ID 4	"Melaphyre" Rhine R., Tamins, Graubünden	3·2	467
ID 5	"Melaphyre" nr. Tamins, Graubünden	8·8	234
ID 6	"Diabase", Ochsenstock, N. of Tödi, Glarus	1·2	40
ID 7	"Diabase", Vorderrötifirn, N. of Tödi, Glarus	1·5	241
B. Turkey—Tertiary basalts			
ID 8	Basaltic lava, Karopinar, Vilâyet Konya	5·3	630
ID 9	Pillow lava, between Ulukisla and Kayseri	9·2	778
ID 10	Basalt, NE of Nigde on rd. to Kayseri	3·3	632
ID 11	Basaltic lava (coarse) Erciyas Dagh, nr. Kayseri	3·4	603
ID 12	Basaltic lava (finer grained) Erciyas Dagh, nr. Kayseri	3·9	334
ID 13	Basalt, Ericyas Dagh, nr. Kayseri	4·2	420
ID 14	Ol. basalt, Sultaniye ovasi, Vilâyet Konya	4·8	480
ID 15	Ol. basalt, Meke Dagh volcano, Vilâyet Konya	5·9	670
ID 16	Ol. basalt bomb, Meke Dagh volcano, Vilâyet Konya	6·3	791

Table 1 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
C. Finland, Pre-Cambrian			
ND 1	Plagioclase porphyrite, Sveco-Fennian, Köyärvi, Sokeslampi	5·4	667
ND 2	Dolerite, Hoskenspää, Brändo, Åland Islands	7·3	435
ND 3	Gabbro, Alatornio, Laivanierni	6·3	782
ND 4	Diabase, associated with rapakivi granite	5·4	490
D. Great Britain			
AD 16	Dolerite (Tertiary), Muckraw, Linlithgow, Scotland	4·1	273
AD 17	Ol. diabase (interstitial analcime) Mauchline, Ayrshire	8·8	551
AD 18	Gabbro, Carrock Fell, England	3·9	241
AD 19	Quartz dolerite, East Lothian, Scotland	7·0	418
AD 43	Ol. dolerite, Scawt Hill, Antrim, Ireland	11·3	257
AD 44	Pyroxene-rich dolerite, Scawt Hill, Antrim, Ireland	14·6	820
	III. India		
A. Archaean basalts			
TD 1	Dolerite, North Arcot dist., Madras	7·1	330
TD 2	Olivine metadolerite, Palamau dist., Bihar	6·8	412
TD 3	Ol. metadolerite, Dudhi Mirzapur dist., U.P.	6·2	407
TD 4	Ol. dolerite, Bicchi	5·5	428
TD 5	Ol. dolerite, dike near Adhaura	6·5	256
TD 8	Dyke rock, Raigarh dist., Madhya Pradesh	3·6	463
TD 11	Metadolerite, Hazaribagh dist., Bihar	7·0	113
B. Mesozoic basalts			
TD 6	Trap (flow) Rajmahal Traps (Jurassic?). Santal, Parganas, Bihar	7·0	181
TD 7	Trap (flow) Rajmahal Traps (Jurassic?), Santal Parganas, Bihar	6·5	209
TD 9	Trap (flow) Rajmahal Traps (Jurassic?), Santal Parganas, Bihar	6·8	220
TD 10	Trap (Vesicular basalt), Deccan (Cretaceous-Eocene), Sangal dist., Madhya Pradesh	6·8	206
TD 14	Trap (flow) Deccan (Cretaceous-Eocene) Kateru, nr. Rajmuhandry	6·3	185
	IV. Africa		
A. Karroo System			
AD 14	Coarse-grained dolerite	7·5	970
AD 15	Coarse-grained dolerite	7·1	565
FD 4	Basalt, Bulawayo dist., S. Rhodesia	6·6	457
FD 6	Basalt (Lava No. 3) Wankie dist., S. Rhodesia	7·6	434
FD 7	Basalt (Lava No. 5) Wankie dist., S. Rhodesia	7·8	330
FD 8	Basalt (Lava No. 1) Wankie dist., S, Rhodesia	7·5	285
FD 9	Basalt (Lava No. 2 Wankie dist., S. Rhodesia	7·5	290
FD 10	Basalt (Lava No. 4) Wankie dist., S. Rhodesia	7·8	344
FD 21	Ol. basalt, borehole, S. Ndanga dist., S. Rhodesia	4·7	746

Table 1 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
B. Bulawayan System (S. Rhodesia)			
FD 1	Carbonated spilitic greenstone, Bubi dist,	9·5	212
FD 2	Limburgite, Bambesi R., Bubi dist.	5·3	91
FD 3	Basaltic greenstone, Belingwe dist.	6·4	25
FD 11	Hornblende-schist, nr. Mayfair mine, Insiza dist.	8·7	132
FD 12	Epidiorite, Shamva, Mazoe dist.	8·0	110
FD 13	Hornblende -schist, Antelope Mine, Matobo dist.	10·1	35
FD 14	Epidiorite, Mazoe dist.	7·5	49
FD 15	Epidiorite, Filabusi, Insiza dist.	7·5	74
FD 16	Epidiorite, Makaha gold belt, Mtoko dist.	10·1	115
FD 17	Basaltic pillow lava, Gwelo dist.	9·3	72
FD 18	Basaltic greenstone, Liverpool mine, Umtali dist.	8·2	45
C. Archaean basalts of the NW Cape			
PD 1	Orthoamphibolite, group 3, main zone of basic rocks, Omkyk anticline	9·0	181
PD 2	Norite, group 1, main zone of basic rocks, Omkyk anticline	9·3	57
PD 3	Metagabbro, group 2, central dome	8·4	300
D. Deweras System (Pre-Cambrian), S. Rhodesia			
FD 5	Basaltic greenstone, Hartley dist.	7·3	454
FD 19	Basaltic greenstone, Lomagundi dist.	7·2	350
E. Lake Kivu Area			
AD 45	Olivine basalt, Lake Kivu, Central Africa	10·4	1126
AD 46	Ol. basalt with Leucite crystals, Lake Kivu	10·6	855
F. Lebombo Volcanics, Swaziland			
LD 1	Porphyrite	1·7	138
LD 2	Limburgite	1·8	142
LD 3	Basalt	5·6	160
LD 4	Basalt	4·4	191
LD 5	Rhyolite	0·89	123
LD 6	Porphyrite	3·1	233
LD 7	Porphyrite	2·2	110
LD 8	Rhyolite?	0·29	125
LD 9	Rhyolite	2·0	74
LD 10	Basalt	6·6	200
LD 11	Basalt	5·4	150
	V. South America		
A. Venezuela			
AD 3	Diabase, Rio Caroni Heres, Bolivar	8·8	176
AD 5	Diabase, Uriman, Bolivar	6·1	182
AD 6	Diabase, Rio Tirika Heres, Bolivar	6·2	143
AD 7	Diabase, Quebrada, Virimbaru Heres, Bolivar	7·6	152
AD 8	Basalt, Pico Maunoir, Alto Orinoco, Terr. Amazonas	6·2	920
AD 9	Daibase, Uriman, Bolivar	7·4	183
AD 10	Diabase, Quebrada, Kuriaraparu Heres, Bolivar	8·2	222

Table 1 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
B. Brazil			
DD 1	Basalt, Triass, or L. Cret., Marechal Floriano, Mata Grande, Alagoas	6·8	80
DD 2	Diabase, Cambrian, Jaburú R, Minas Gerais	4·4	630
DD 3	Diabase, L. Triass., Triângulo Mineiro, Minas Gerais	5·2	280
DD 5	Basalt, Rio Pardo, Rio Grande do Sul	5·7	176
DD 6	Diabase, Urussanga, Santa Catarina	8·0	259
DD 7	Basalt, Porto Uniáo, Paraná	7·9	722
DD 8	Diabase, Ribeira do Iguape, São Paulo	6·8	375
DD 9	Diabase, Jaguariaiva, Paraná	7·5	356
DD 10	Basalt, Recife, Pernambuco	8·2	805
DD 11	Diabase, Terezina, Piauí	5·1	564
DD 12	Augite-Tonalite, Tijuca, Distrito Federal	5·2	1671
DD 13	Ankaratrito, Ilha Fernando Noronha	9·2	1131
DD 14	Basalt, Bôa Vista, Amazonas	6·9	202
DD 15	Quartziferous gabbro, Aicarem, Amazonas	6·9	164
DD 16	Diabase, Bôa Vista, Amazonas	6·4	380
	VI. North America		
A. Eastern United States			
1. *North Carolina metabasalts (Early Palaeozoic?)*			
a. Related to Bakersville Dike Swarm			
MD 1	Porphyroblastic	5·2	384
MD 2	Fine-grained	5·9	211
MD 3	Coarse-grained	6·8	300
MD 4	Coarse-grained	7·4	242
MD 5	Fine-grained	6·2	370
MD 6	Fine-grained	6·6	521
MD 7	Orthopyroxene rock	6·3	254
b. Amphibolites of Roan formation			
BK 303			315
BK 304			133
BK 305			117
BK 306			56
BK 307			37
BK 308			90
BK 309			133
BK 310			270
c. Amphibolites of uncertain origin (see text)			
MD 8	Hornblende, biotite, garnet, plagioclase schists, and gneisses	6·7	524
MD 9		6·6	606
MD 10		7·1	424
MD 11		7·4	445
MD 12		6·7	495
MD 13		7·3	397
MD 14		6·7	457
MD 15		5·3	480

Table 1 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
2. *Triassic basaltic rocks*			
AD 95	Diabase, Gulf Mills, Montgomery Co., Pa.	7·7	110
AD 97	Diabase, Radnor Twp., Pa.	7·7	78
AD 98	Diabase, Conshocken, Pa.	8·3	174
AD 99	Diabase, Frankford, Pa.	6·0	43
AD 100	Diabase, Big Hill, Cornwall, Pa.	7·9	122
AD 101	Granophyric Diabase, Round Top, Gettysburg, Pa.	7·6	131
AD 102	Diabase, South Mt., York Co., Pa.	6·0	189
AD 106	Diabase, Leesburg, Loudon, Co., Va.	7·2	160
AD 107	Ol. diabase, Charlotte, N. Carolina	7·2	36
AD 108	Diabase, First Watchung, Paterson, New Jersey	7·2	123
AD 109	Basalt, Second Watchung, Haledon, New Jersey	7·1	108
AD 110	Diabase, Snake Hill, New Jersey	6·4	127
AD 116	Diabase, Mt. Holyoke, Mass.	8·5	158
AD 119	Diabase, Hartford, Conn.	5·7	201
AD 120	Diabase, Woodbury, Conn.	6·5	177
W 1	Diabase, nr. Centerville, Fairfax Co., Va.	11·0	158
3. *Pre-Triassic basaltic rocks*			
AD 88	Gabbro (coronite), Peekskill, New York	6·8	407
AD 90	Diabase, Trembleau Pt., Lake Champlain, New York	6·8	993
AD 91	Diabase, Cascadeville, New York	7·1	1627
AD 93	Diabase, Thousand Islands, New York	6·8	205
AD 96	Quartz diorite, Philadelphia, Pa.	7·0	230
AD 103	Dolerite, Iron Hill, S. of Newark, Del.	10·6	35
AD 104	Gabbro, diorite, Mt. Hope, Md.	7·0	249
AD 105	Gabbro, Ilchester, Md.	7·9	76
AD 112	Diabase, Asncore Mt., Mt. Desert Isle, Me.	7·1	325
AD 113	Quartz Diabase, Addison, Me.	5·8	188
AD 114	Diabase, Sommerville, Mass.	6·3	579
AD 115	Diabase (gabbro?) Nahant, Mass.	6·5	670
AD 117	Dike rock (diabase?) Crawford Notch, N.H.	5·6	694
AD 121	Gabbro, Ascutney Notch, Vt.	6·4	1062
4. *Adirondacks*			
AD 86	Norite, Westport, New York	8·8	674
AD 87	Anorthosite, Elizabethtown, New York	8·8	1025
AD 89	Anorthosite, Euba Mills, New York	8·1	1010
AD 92	North Hudson, New York	8·1	967
B. Midwestern and Canadian Pre-Cambrian			
1. *Keweenawan rocks of Lake Superior Region*			
AD 63	Olivine diabase, nr. S. Porcupine, Ontario, Can.	6·1	697
AD 64	Gabbro, Tatlock, Ontario	5·5	350
AD 65	Basalt, Isle Royal, Mich.	5·4	462
AD 66	Quartz diabase, Lighthouse Pt., Marquette, Mich.	7·4	142
AD 69	Gabbro, Beaver Bay, Minn.	5·9	519
AD 70	Ol. diabase, Beaver Bay, Minn.	7·6	305

Table 1 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
1. *Keweenawan rocks of Lake Superior Region* (*continued*)			
AD 71	Ol. gabbro, Beaver Bay, Minn.	7·1	358
AD 72	Diabase, Beaver Bay, Minn.	6·6	354
AD 73	Diabase, Grand Marais, Minn.	6·6	167
AD 83	Anorthosite, Minneapolis, Minn.	9·3	735
AD 84	Ol. Diabase, Grand Portage, Minn.	6·3	305
2. *Duluth Gabbro*			
AD 74	Red Rock contaminated by early anorthosite	6·1	405
AD 75	Anorthosite (upper facies)	7·6	481
AD 76	Aplitic red rock	3·2	319
AD 77	Main mass of banded Gabbro	5·3	289
AD 78	Gabbro (above banded gabbro, below anorthosite)	6·1	191
AD 79	Basal gabbro (?)	7·7	410
AD 80	Gabbro (at floor) contaminated by basalt hornfels	5·4	258
AD 81	Pegmatitic mass at base of Duluth gabbro	9·5	208
AD 82	Average ol. gabbro (near base)	6·8	416
3. *Keewatin Age*			
GB 1	Pillow lava, Canada	—	98
C. *Western United States* (*except Pacific Northwest*)			
1. *Beartooth Range, Montana*			
BD 14	Diabase dikes cutting granitic gneiss of the area	4·2	22
BD 16		4·6	118
BD 18		5·0	147
BD 20		5·6	128
BD 22		4·8	403
BD 24		6·1	145
2. *Other basaltic rocks*			
AD 67	Diabase, Squaw Creek, Black Hills, S.D.	6·9	295
AD 68	Gabbro, Black Hills, S.D.	6·2	415
AD 48	Basalt, American Ravine, Silver City, Nev.	8·6	1825
AD 49	Diabase, Humboldt Range, Nev.	7·5	1235
AD 57	Basalt, Comstock, Nev.	6·7	1023
AD 58	Diabase, Soap Hill, Nev.	3·4	316
UD 4	Basalt? (Pliocene or Pleistocene) Shoshone Range, Crescent Valley Quad, Nev.	2·4	271
AD 50	Diorite, Mosquito Range, E. of Leadsville, Colo.	4·8	779
AD 51	Gabbro, Hermosa Park, Colo.	5·8	1875
AD 52	Dolerite, N. Table Mts., Golden, Colo.	6·1	991
AD 54	Diorite, dike W. of Spanish Peaks, Colo.	4·4	1029
AD 55	Ol. gabbro, Cripple Creek, Colo.	4·9	735
AD 56	Quartz gabbro, Iron Hill, Colo.	5·6	209

Table 1 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
2. *Other basaltic rocks* (*continued*)			
AD 59	Quartz basalt, Lassen Peak, Calif.	5·3	448
AD 60	Ol. basalt, Truckee, Calif.	4·9	1835
AD 61	Ol. basalt, Jamestown, Tuolumne Co., Calif.	5·3	675
AD 62	"Anorthite-gabbro", nr. Nevada City, Calif.	10·7	400
AD 41	Basalt, Las Esperanzas, Mexico	7·6	700
AD 42	Basalt, Ebano, nr. Tampico, Mexico	10.2	1010
D. Pacific Northwest			
1. *Clarno formation* (*Eocene*): *andesites and basaltic andesites*			
QD 36	Basaltic andesite dike	6·1	434
QD 37	Andesite flow	6·9	276
QD 41	Hypersthene basaltic andesite from the Sheep Rock Plug	4·9	535
QD 42	Olivine andesite flow	5·0	238
QD 43	Basalt flow	6·0	645
QD 44	Basaltic andesite	3·5	296
QD 45	Dacite (?) flow—or else a glassy andesite	5·0	428
2. *Columbia R. tholeiitic basalts* (*Miocene*)			
QD 1	Waterville, Wash.	5·7	292
QD 2	Dike, Grande Ronde river, S. of Anatone, Wash.	4·5	240
QD 3	2nd flow from top nr. Trinidad, Wash.	6·9	244
QD 4	10th flow from top nr. Trinidad, Wash.	6·1	290
QD 5	First flow from top nr. Yakima, Wash.	7·5	204
QD 6	8th flow from top nr. Yakima, Wash.	5·9	335
QD 7	Wallula Gap, nr. Pasco, Wash.	5·6	292
QD 10	Snake R. Canyon, nr. Lewiston, Idaho	7·8	248
QD 13	Salmon R., nr. Cottonwood, Idaho	5·6	385
QD 16	Grande Ronde Canyon, nr. Anatone, Wash.	5·1	352
QD 22	Lawyers Canyon, Grangeville plateau, Idaho	5·2	366
QD 23	Basal flow in Pine Creek section, NE Oregon	7·4	284
QD 24	La Fleur, Oregon	5·6	315
QD 25	Rock Island dam, Wash.	6·0	336
3. *Olivine basalts* (*Pliocene-Recent*)			
QD 26	Rimrock flow, W. of Prineville, Oregon	6·3	320
QD 27	Horse Ridge, SE of Bend, Oregon	6·5	814
QD 28	Diktytaxitic flow, W. of Hood R., Oregon	6·9	825
QD 29	Simcoe Mt., W. of Satus Pass, Wash.	7·1	566
QD 30	Satus Pass, Wash.	7·4	685
QD 31	Porphyritic flow, Abert Rim, Oregon	8·4	484
QD 32	Goldendale, Wash.	7·1	500
QD 33	Flow interstratified in the Dalles fm., nr. Mecca, Ore.	4·4	581
QD 34	Recent ol. basalt, Roberts, Oregon	6·8	1059
QD 35	"The Big Lava Flow" near Willard, Wash.	6·4	362

Table 1 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
	VII. Other Rocks		
A. The Rocks of the Oslo Region, Norway			
JD 1	Pryoxenite	11·7	300
JD 2	Essexite, normal	6·7	527
JD 3	Foyaite, husebyite	1·3	1467
JD 4	Essexite, Platy flow structure	6·4	464
JD 5	Olivine gabbro-diabase, subvolcanic	5·1	904
JD 6	Akerite	4·3	510
JD 7	Windsorite, apophysis in Silurian beds	1·1	440
JD 8	Rhomb-porphyry 1	3·6	1481
JD 9	Nepheline syenite, foyaite	1·1	62
JD 10	Nordmarkite (half) porphyric	0·95	266
JD 11	Essexite-porphyrite (basalt)	6·9	788
JD 12	Kjelsåsite	4·0	1011
JD 13	Anorthosite (Modumite) Hovlandite (?)	9·8	866
JD 14	Larvikite	3·7	585
JD 15	Dyke of rhomb-porphyry	3·2	601
JD 16	Camptonite (dyke)	7·5	760
JG 1	Na granite, Ekerite	0·23	6
JG 2	Granitite	0·59	24
B. Miscellaneous			
AD 20	Ol. basalt, Wannow, Bohemia	8·6	1600
AD 40	Ol. basalt, San Cristobal, Santo Domingo, Haiti	7·5	356
AD 47	Gabbro (norite) massif of Mt. Kakoulima, Fr. Guinea	7·6	1353
AD 111	Anorthosite, Ste. Marguerite, nr. Montreal, Canada	8·2	785
GG 9	Lamprophyre, Sagamaga Lake, Ontario, Canada	7·0	700
GG 31	Gabbro, nr. Messina, Transvaal, Africa	10·0	145
OD 1	Ol. gabbro (Tertiary) Sooke Peninsula, Vancouver, B.C.	10·4	136
OD 2	Ol. gabbro (Tertiary) Sooke Peninsula, Vancouver, B.C.	6·6	163
OD 3	Basaltic rock, massive, Vancouver group, B.C.	8·1	284
QD 48	Andesite flow (Pleistocene), Prineville-Pauline area, C. Oregon	4·4	440
QD 49	Andesite dike (Pleistocene), Prineville-Pauline area, C. Oregon	5·3	412
AG 2	Basic Charnockite, St. Thomas Mt., Madras, India	6·9	155

Table 2. Granitic rocks

Number	Description	Precentage Ca	p.p.m. Sr
	I. Canadian Shield		
AG 58	Granite, Tory Hill, Ontario	0·66	204
AG 59	Granite, Glamorgan batholith, Haliburton, Ont.	0·69	151
AG 60	Granite, Redol R., N. of Lake Superior	0·76	103
GG 1	Pink granite, Lyndhurst, Ontario batholith	0·85	219
GG 2	Pink granite (edge), Lyndhurst, Ontario batholith	1·1	357
GG 3	Pink granite, isolated stock assoc. w. Lyndhurst batholith	0·71	194
GG 4	Killarney granite (N. of L. Huron), Serpent R.	1·1	196
GG 5	Killarney granite, Spragge-Cutler, Ontario	1·5	329
GG 6	Pink Killarney granite, Brick Lake, Webbwood, Ont.	0·21	126
GG 7	Pink granitic gneiss, shore of Collins Inlet	0·45	277
GG 8	Coarse pink porphyritic granitic gneiss, N. of Collins Inlet	1·1	275
GG 10	Laurentian (?) granite, U. Rice Bay of Rainy Lake	1·9	810
GG 11	Grey granite, Rice Bay of Rainy Lake	1·4	754
GG 12	Quartz diorite, S. of Goose Is., Lac Seul	4·6	695
GG 13	Grey granite, between Lac Seul and Grassy Lake	3·0	335
GG 14	Pink granite, drill core, Stony Mountain, N.W. of Winnipeg.	0·54	128
GG 15	Gneissoid chlorite granite, Assizes Is., Labrador	1·0	151
GG 16	Pine granite, Lady Bight, Labrador	1·2	163
GG 17	Brownish-red granite, Menifield Bay, Labrador	1·6	192
GG 18	Coarse pink granite, W. side of Alliuk Bight, Labrador	2·7	683
GG 19	Grey gneissic granite, Pigeon Island, Indian Harbor, Labrador	1·6	471
GG 20	Pine-grey granite, Red Sucker L., N. of L. Winnipeg	0·82	81
GG 21	Pink-grey granite, Gods Lake, Manitoba	2·0	421
GG 22	Red granite nr. contact of paragneiss 65° 45′ N, 112° 45′ W	0·35	51
	II. United States		
A. Rocky Mountain Area			
AG 12	Granite (coarse-grained) The Siding, Wyoming (Laramie Range)	0·92	59
AG 13	Biotite-hornblende granite, typical Sherman granite, Laramie Range	1·6	112
AG 14	Archaean granite, The Siding, Wyoming	0·45	42
AG 15	Granite, Rattlesnake Range, Natrona Co., Wyoming	3·2	649
AG 16	Archaean granite, Silver Crown, Laramie Co., Wyoming	1·2	218
AG 17	Graphic granite, Whalen Canyon, Laramie Co., Wyoming	0·22	42
AG 18	Granite, Rich Creek, Atlantic City, Wyoming	2·9	583
AG 19	Diorite, Rambler Mine, Wyoming	5·4	612
AG 39	Granite, Georgetown, Colorado	2·1	298
AG 40	Gneissoid granite, Front Range, Boulder Co., Colorado	1·8	655
AG 41	Biotite granite, Platte Canyon, Jefferson Co., Colorado	0·75	35
AG 42	Granite, summit of Pike's Peak, Colo.	0·84	59
AG 48	Granite, Santa Fe, New Mexico	0·82	92
AG 75	Granite, Boulder River, Montana	1·4	330
AG 76	Granite, First divide W. of Helena, Mont.	1·9	944
AG 77	Basic granite, "Butte granite," Butte, Mont.	2·4	517

Table 2 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
B. Western United States, Mesozoic			
AG 22	Granite Mojave Mts., Colorado R., Arizona	0·68	170
AG 23	Quartz diorite, nr. Tombstone, Arizona	1·2	295
AG 29	Boulder batholith granite	2·6	442
AG 30	White granite, Little Cottonwood, Utah	0·72	27
AG 31	Granite, Independence Rock, Utah	1·1	515
AG 32	Granite, Gibraltar Pass, Ledge Mts., Utah	1·1	225
AG 35	Hornblende-biotite granodiorite, Gold Hill, Toole Co., Utah	3·1	661
AG 37	Quartz monzonite, Carson City, Nevada	2·9	527
AG 50	Granite, Austin, Nevada	1·6	383
AG 51	Diorite, Mt. Davidson, Virginia City, Nev.	2·1	690
AG 52	Granite, East branch of Sierras, facing Reno, Nevada	0·71	42
AG 55	Granite, Rocklin, Placer Co., Calif.	1·3	417
AG 56	Granite, Coast Range, N. of San Francisco, Cal.	0·58	33
AG 57	Monzonite, Squaw Peak, Placer Co., Calif.	3·3	585
AG 80	Granite, Leesburg, Idaho	0·82	24
OG 1	Saanich granodiorite—a facies of Coast Range batholith, Corvichan Lake, southern Vancouver Island, B.C.	2·2	274
OG 2		1·6	115
OG 3		0·46	94
OG 4		4·3	572
OG 5	Salmon River stock (Monzonite), East end	6·3	1127
OG 6	Salmon River stock (Monzonite), Center	5·9	1093
AG 7	Granodiorite, Colville batholith, Osozoos Quad., Wash.	2·7	348
C. New England Granites			
1. *Maine*			
AG 92	Granitic gneiss, Clarks Islands	1·1	41
AG 93	Red Felspathic Granite, Great Duck Is. nr. Mt. Desert	0·37	24
AG 95	Granite gneiss, nr. Leeds Center, Androscoggin Co.	1·1	177
AG 96	Granite, Deer River	1·1	163
AG 97	Granite (Riebeckite), Mt. Agamenticus	0·29	28
AG 98	Granite, Red Beach	0·57	37
AG 99	Red granite, Stony Creek	0·44	6
AG 100	Granite, Kennebunkport	0·37	29
AG 101	Granite, Round Point	1·3	797
AG 102	White granite, Frenchman's Bay	0·93	91
AG 103	Granite porphyry, Ratcliffe Island	0·87	23
2. *Massachusetts*			
AG 104	Braintree granite, Pine Hill Quarry, Braintree	0·11	37
AG 105	Granite, nr. S. Weymouth	1·3	537
AG 106	Granite, Weymouth	0·67	320
AG 107	Red granite, Rockport, Mass.	0·41	14
AG 108	Granite, Bay View, Lanesville, Cape Ann	0·49	14

Table 2 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
2. *Massachusetts* (*continued*)			
AG 109	Grey granite } Rockport Granite Co., Rockport	0·16	6
AG 110	Pink granite } Rockport Granite Co., Rockport	1·2	218
AG 111	Green granite } Rockport Granite Co., Rockport	0·59	10
AG 114	Fine granite, Weymouth Fire R., Weymouth	0·59	42
AG 115	Granite, Rattlesnake Hill nr. Boston	0·33	15
AG 116	Pink granite, Milford	0·57	17
AG 117	Granite, nr. New Bedford	0·47	56
AG 118	Fine-grained granite, W. Dedham	0·49	108
AG 119	Granite, Somerville	0·52	11
AG 120	Williamsburg granodiorite, Northampton	3·2	920
AG 121	Granite, Chester	1·4	678
AG 129	Granite (peralkaline) Peabody Stock, Essex Co.	0·79	72
AG 130	Granodiorite, Phillips Pt., Essex Co.	0·52	47
3. *Rhode Island*			
AG 122	Granite, Westerly	0·54	213
G1	Granite, Smith Granite Co., Westerly	1·0	218
4. *New Hampshire*			
AG 124	Granite, walls of flume, White Mts.	0·31	38
AG 125	Biotite granite, Conway	0·89	28
AG 126	Muscovite-biotite granite, Haverhill	2·4	664
AG 127	Granitic gneiss "Bethlehem granodiorite," Bethlehem	1·2	152
AG 128	Granite, Fitzwilliam	0·89	71
5. *Connecticut*			
AG 131	Granitic gneiss (phase of Glastonbury), Tower Hill, Glastonbury	1·2	349
AG 132	Granite, Stony Creek	0·96	307
AG 133	Killingworth granite, nr. Killingworth	2·4	706
AG 134	Granite, Plymouth	1·3	565
6. *Vermont*			
AG 135	Granite, Brattleboro	0·80	211
AG 136	Biotite granite, Ascutney Mtn.	0·83	354
D. Eastern United States			
AG 81	Granite, Elizabethtown Quad., Adirondacks, N.Y.	0·57	15
AG 82	Granite, Peekskill, New York	1·0	745
AG 83	Mt. Adam granite, Goshen Quad., N.Y.	0·96	466
AG 84	Hornblende granite, Anthony's Nose, Easton, Pa.	0·58	104
AG 85	Granite, Woodstock, Maryland	1·1	914
AG 86	Granite, Mt. Airy, North Carolina	1·4	980
AG 87	Granitic gneiss, Raleigh, North Carolina	1·2	104
AG 88	Gneiss granitite, Columbia, South Carolina	1·4	389
AG 89	Granite, Charlotteburg, North Carolina	1·5	609
AG 90	Granite, Black Ledge, Georgia	0·83	67
AG 91	Granite, Little Stone Mtn., Georgia	0·77	19

Table 2 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
E. Middlewestern United States			
AG 61	Granite, Burnet Co., Texas	2·1	682
AG 62	Granite, nr. Austin, Texas	0·49	26
AG 63	Granite, Burnet Co., Texas	0·96	38
AG 65	Granite, Wausau, Wisconsin	0·54	23
AG 66	Granite, Montello, Wisconsin	0·91	29
AG 68	Pink granite, Snowbank Lake, Minn.	1·0	590
AG 69	Saganaga granite, N. of Gunflint Lake, Minn.	1·0	701
AG 70	Granite (porphyritic) Rockville, Minn.	1·5	294
AG 71	Grey hornblende granite, East St. Cloud, Minn.	1·6	1045
AG 72	Red hornblende granite, East St. Cloud, Minn.	0·74	98
AG 73	Granite, Iron Mt., Missouri	0·58	15
	III. Fenno-Scandian Shield		
NG 1	Granite, Åva, Brando, Åland Islands	0·69	366
NG 2	Red gneissose granite, Sveco-Fennian, Urjula, Lintula	0·41	91
NG 3	Microcline porphyric gneissose granite, Sveco-Fennian, Tammela, Saloisjarvi	1·6	258
NG 4	Granodiorite, Sveco-Fennian, Jokioinen, Nummela	3·2	584
NG 5	Hetta granite, Karelian synkinematic, Porrastrenturi	1·6	208
NG 6	Karelian synkinematic granodiorite	3·7	546
NG 7a	Granite boulder from basal conglomerate, Karelian fm., Saarijarvi	2·8	351
NG 8	Granodiorite, Alatornio	2·3	740
NG 9	Microcline granite, Sveco-Fennian	0·65	77
NG 10	Garnet-bearing, microcline granite, Sveco-Fennian	0·66	71
NG 11	Pegmatite, Simo, Simoniemi, Viitala	0·085	419
NG 13	Microcline granite, Sveco-Fennian, Pernio	0·22	23
NG 14	Microcline granite, Simo, Malesniemi	0·64	465
NG 15	Rapakivi, Lemi, Taipole	2·5	127
NG 17	Kuru granite, Sveco-Fennian	1·2	299
NG 18	Microcline granite, Sveco-Fennian	1·5	263
NG 19	Muscovite-microcline granite, Sveco-Fennian	0·73	69
	IV. Africa		
AG 25	Rapakivi granite, Gaberones, Bechuanaland	1·9	70
AG 26	Mahalapye granite, Bechuanaland	1·4	92
AG 27	Bushveld granite	0·41	37
AG 28	Vredeforte granite	1·11	311
GG 23	Young granite, Kalulushi, Northern Rhodesia	0·20	135
GG 24	Young granite, Mivekera, Northern Rhodesia	0·59	118
GG 25	Young granite, N'Dola, Northern Rhodesia	1·48	447
GG 26	Old granite, Mutondo, Northern Rhodesia	0·29	32
GG 27	Old granite, Gutu, Southern Rhodesia	0·78	94
GG 28	Old granite, Mudzi R., Southern Rhodesia	0·81	65
GG 29	Old granite, S. of Bulawayo, Southern Rhodesia	1·4	170
GG 30	Old granite, nr. Salisbury, Southern Rhodesia	0·78	94
GG 32	Older granite gneiss, nr. Pietersburg, Transvaal	1·0	304
GG 33	Older granite gneiss, nr. Pietersburg, Transvaal	1·2	470

Table 2 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
	IV. Africa (*continued*)		
GG 34	Young granite, drill hole, nr. Magnet Hts., Bushveld, Transvaal	0·49	77
GG 35	Old granite, Pretoria-Johannesburg, Transvaal	0·87	155
GG 36	Old granite gneiss, Hlatikula, Swaziland	0·66	43
	V. Other Granites		
A. Great Britain			
AG 4	Granite, Loch Etive, Argyllshire, Scotland	1·8	560
AG 5	Granophyre, Carrock Fell, England	1·6	137
AG 6	Shap granite, Westmorland, England	1·3	515
AG 10	Fine-grained granodiorite, Newry, North Ireland	2·1	514
AG 11	Granodiorite, Slieve Garron, Newry, North Ireland	3·2	856
B. Mexico			
AG 8	Diorite, Canyon de las Animas, Perdidas	5·1	280
C. Puerto Rico			
EG 1	Granites and diorites from Adjuntas-Utuado area	1·8	461
EG 2		2·9	454
EG 3		2·8	234
EG 4		4·0	569
EG 5		4·1	545
EG 6		2·9	591
	VI. Rhyolites		
AG 20	Western rim of Grand Canyon of Yellowstone R., Yellowstone Park	0·06	204
AG 21	Golden Gate, Yellowstone Park, Wyoming	0·24	23
AG 33	Simpson Pass, Utah	0·19	40
AG 34	S. end of Hawawa Range, Utah	1·0	24
AG 36	Hartford Hill, Silver City, Nev.	4·3	248
AG 38	S. of Gov. Bradley Mine, Humboldt Range, Nev.	0·039	62
AG 43	Woody Creek, Aspen, Colo.	0·17	30
AG 44	Red Rhyolite, San Juan Mts., Ouray Co., Colo.	0·19	788
AG 46	Leadville, Colo.	1·4	402
AG 47	Pyramid Peak, New Mexico	0·36	19
AG 49	S. side of Carson Desert, Nevada	0·58	95
AG 53	Ruby Hill, Nevada	0·22	38
AG 54	El Dorado Canyon, Calif.	0·51	109
AG 64	S. E. Terry's Peak, Black Hills, S.D.	0·086	50
AG 67	Baraboo Range, Lower Narrows, Baraboo R., Wisc.	0·045	30
AG 74	Shannon Co., Missouri	0·21	50
AG 78	Little Belt Mts., Mont.	1·0	·1605
AG 79	Rhyolite Hill, N. of Butte, Mont.	2·2	1195
AG 94	Great Cranberry Island, Maine	0·89	248
AG 112	Blue Hills Park, nr. Boston, Mass.	0·21	50
AG 123	Ammonoosuc rhyolite. Lisbon, N.H.	0·38	48
QG 1	Welded rhyolite tuffs (Oligocene), John Day fm., Pac. Northwest	0·21	29
QG 5	Sintered rhyolite tuff, John Day fm., Pac. Northwest	0·43	18

Table 3. Shales

Number	Description	Percentage Ca	p.p.m. Sr
	I. Palaeozoic		
A. Cambrian			
AS 23	Shale w. Olenellus, L.E., Weymouth, Mass.	0·10	245
AS 24	Upper E., St. John, New Brunswick	0·079	321
AS 25	St. Albans shale, Albertan, Georgia Plains, Vt.	0·76	336
AS 26	Watauga shale, M.E., Roanoke Co., Va.	0·11	164
AS 27	Bonne Terre shale, Elvins, Missouri	16·1	237
B. Ordovician			
AS 1	Martinsburg shale, Chazyan, Westlawn, Pa.	0·17	233
AS 2	Athens shale w. graptolites, Normanskill, Roanoke, Virginia	0·036	487
AS 3	Deer R. shale, Trenton-Collingwood or Gloucester, Copenhagen, New York	1·3	412
AS 4	Thebes shale, Richmond, Cape Girardeau, Misssouri	1·1	357
AS 5	Hudson R. shale, Kingston, N.Y.	2·8	478
AS 6	Utica shale, Utica, New York	5·3	528
AS 7	Hudson R. shale, Lorraine, Martins Creek, Pa.	0·050	255
AS 8	Reedsville shale, L. Cincinnatian, Jonesville, Va.	0·86	373
AS 9	Frankfort shale, Chavwick, nr. Utica, N.Y.	2·1	275
AS 10	Orchard Creek sh., Cape Girardeau, Mo.	1·6	533
AS 11	Shale w. Triarthrus, Frankfort, Washington Mills, New York	2·4	337
AS 12	Maquoketa sh. Cincinnati-Richmond, Graf, Iowa	9·9	579
C. Silurian			
AS 13	Walcott sh., Niagara-Clinton, Rochester, N.Y.	7·5	461
AS 14	Sodus sh., Clinton, Rochester, N.Y.	0·41	348
AS 15	Williamson sh., U. Clinton, Rochester, N.Y.	6·4	410
AS 16	Rochester shale, Middleport, N.Y.	8·5	377
AS 17	Shale, phosphatic nodules, and iron ore, Bennet Quarry, Clinton, New York	2·1	204
AS 18	Waldron sh., Niagaran, Tunnel Mill, Vernon, Ind.	13·2	341
AS 19	Medina sh. (Basal Sil-U Ord?) Goes, Greene Co., O.	5·7	337
AS 20	Longwood sh. (green facies), Water Gap, Pa.	0·26	237
AS 21	Black sh., M. Shawangunk, Del. Water Gap, Pa.	0·037	223
AS 22	Red sh., High Falls, Salinan, High Falls, N.Y.	0·79	218
D. Permian			
AS 30	Helderbergian, L. Mempremagog, Quebec	20·4	959
AS 31	Heragon sh., nr. Dougherty, Murray Co., Okla.	19·6	463
AS 32	Frog Mt. sh., Oriskanian, Ragland, Alabama	5·6	109
AS 33	Esopus sh., Becraft Mt., N.Y.	0·15	116
AS 34	Marcellus sh., Catskill Region, N.Y.	17·2	617
AS 35	Marcellus sh., Hamilton, Stroudsburg, Pa.	1·9	223
AS 36	Carbonaceous sh., Ashokan, Summitville, N.Y.	0·15	141
AS 37	Mt. Marion sh., Erian-Hamilton, Kingston, N.Y.	9·3	315
AS 38	Huron sh., Lewis Center Run, Ohio	2·9	159

Table 3 (*continued*)

Number	Description	Percentage Ca	p.p.m. Sr
D. Permian (*continued*)			
AS 39	Snider Creek sh., Calloway Co., Mo.	20·0	479
AS 40	Genesee sh., Hamilton, 18 mi. Creek, N.Y.	10·4	229
AS 41	Oneonta sh., U. Dev., Senecan-Portage, Ashokan Dam N.Y.	3·9	113
AS 42	Cashaqua sh., Portage, Cashaqua Creek, Livingston Co., N.Y.	0·75	177
AS 43	Marcellus-Genesee sh., Roanoke Co., Va.	16·1	394
AS 44	Ohio (Huron) black sh., Portage, Huron Creek	0·51	102
AS 45	Conodent sh., Uppermost Dev., Cayahoga Co.	0·33	209
AS 46	Blue shale, Genesee, Mt. Morris, N.Y.	2·5	199
AS 47	Catskill shale, Pottsville, Pa.	0·14	124
AS 48	Brailler shale, Chautauquan, Roanoke Co., Va.	0·24	125
AS 49	Woodford sh., Woodford, Oklahoma	1·4	181
AS 50	Chattanooga sh., Sale Creek, Tenn.	0·37	133
AS 52	Eureka sh., Chattanooga, Spavinaw, Okla.	0·21	52
AS 53	Sulphur Springs sh., St. Genevieve Co., Mo.	9·7	190
AS 54	Olentangy sh. (U. Dev.), Delaware, Ohio	15·1	68
E. Mississippian			
AS 55	Bluefield, Stony Ridge Gap, W. Va.	19·6	248
AS 56	Warsaw, Keokuk, Iowa	17·1	119
AS 57	Cayahoga, Vernon, Ohio	0·39	73
AS 58	Orangeville (Sunbury) sh., Cortland, Ohio	0·14	28
AS 59	Floyd sh., Meramecan, Bessemer, Ala.	0·11	172
AS 60	Gasper sh., Chesterian, Cherokee, Ala.	0·75	132
AS 61	Red sh., Mauch Chunk, Hazelton Quad, Pa.	0·10	99
F. Pennsylvanian			
AS 62	Allegheny, Clearfield, Pa.	0·14	140
AS 63	Graphitic sh., Rhode Is. fm., Newport Neck, R.I.	0·11	345
AS 64	Red sh., Lower barren coal measure, Carrol Co., Ohio	0·11	1513
AS 65	Shale w. pelecypods, carbonic	5·0	277
AS 66	Warren group, Grand View Pike, Spring City, Tenn.	0·08	111
AS 67	Varved metashale, Newport Neck, R.I.	0·92	182
AS 68	Lower Smithwick sh., Bend, San Saba Co., Texas	20·4	441
	II. Mesozoic		
A. Triassic			
AS 69	Neward shale, Granton, N.J.	2·4	299
B. Cretaceous			
AS 28	Mowry sh., Gulfian, Hutton Lake, Wyo.	0·50	167
AS 29	Fuson sh., Comanchean, Sheep Mt., Wyo.	13·9	320
AS 70	Eagle Ford sh., Austin, Texas	15·8	748

Table 4. Schists

Number	Description	Percentage Ca	p.p.m. Sr
AP 1	Berkshire schist, Mt. Prospect, Salisbury, Conn.	0·47	417
AP 2	Kyanite mica schist, Hartford, Conn.	0·20	189
AP 3	Garnetiferous hornblende schist, Orange, Conn.	4·3	230
AP 4	Mica schist, Watertown, Conn.	1·6	300
AP 5	Schist with magnetite, Stockbridge, Vt.	0·56	298
AP 6	Actinolite talc schist, Stockbridge, Vt.	3·5	89
AP 7	Staurolite schist w. biotite and garnet, Jordan Falls, Nova Scotia	0·24	262
AP 8	Biotite schist, New Bedford, Mass.	1·4	152
AP 9	Phlogopite schist, Montville, N.J.	9·3	123
AP 11	Talc schist w. magnetite, Marquette Co., Mich.	0·18	257
AP 12	Chlorite schist, Silver City, Nevada	0·53	525
AP 13	Glaucophane schist, Morgan Hill, Calif.	2·6	59
AP 14	Mica schist, Cripple Creek, Colo.	0·03	271
AP 15	Calcitic chlorite schist, Carlon Co., Wyo.	3·4	93
AP 16	Chlorite schist, Black Hills, S.D.	7·1	329
AP 17	Mica schist, Santa Fe, N. Mexico	0·19	173
AP 18	Biotite-diorite schist, Wasatch Mts., Utah	6·4	187
AP 19	Green schist, Yiojarvi, Finland	6·4	497
AP 20	Sericite schist, Salair, U.S.S.R.	5·4	302
AP 21	Hornblende schist, New York City	6·4	229
AP 22	Hornblende schist, Philadelphia, Pa.	7·1	112
AP 23	Anthophyllite schist, Bare Hills Copper Mine, Md.	1·2	44
AP 24	Garnetiferous hornblende schist, Cap a l'Aigle, Quebec	0·09	24
AP 25	Schist, Ariege, France	5·2	636

calcium and parts per million strontium. The numbers refer to the Lamont rock-collection code system. Additional data concerning the samples can be obtained from the authors. All samples have been run at least in duplicate, and may be considered to have an error of $\pm 17\%$ for values of Sr lower than 100 p.p.m. and $\pm 9{\cdot}8\%$ for higher Sr values at the 95% confidence interval.

Some of the specimens of granitic rocks were chips from collections where large samples were not available. Although an attempt was made to take as large a fraction as possible, there is undoubtedly some error of sampling for some of the coarser-grained rocks.

There are two ways in which to treat the discussion of a trace element. One method involves a discussion of the distribution of the trace element in various geologic systems, with no particular regard to any other element. A second method is to relate the trace element to a major element with which it has natural affinities. This latter method has proved useful for strontium when compared to calcium. An attempt to find any significant or useful correlation of potassium and strontium proved abortive. Consequently, neither potassium nor any other of the major rock-forming elements except calcium are used as reference points for the discussion of the geochemistry of strontium. The abundance of calcium in a rock is governed

by the composition and the total amount of calcium-bearing minerals. To a first approximation, the mineral group responsible for both the calcium and strontium content of a silicate rock is the feldspar group. The importance of certain pyroxenes and amphiboles should undoubtedly be considered in an expanded study of the distribution of strontium and calcium in coexisting minerals.

For the benefit of a synthetic discussion, a further simplification was necessary. Two major silicate rock-types are discussed: basaltic rocks and granitic rocks. Where andesites occur and are known to have basaltic affinities, they are included under the classification of basaltic rocks. On the other hand, a few dioritic rocks with obvious granitic associations, though having the same chemical composition as andesites, are included under granitic rocks. The log Ca vs. log Sr curves for basaltic rocks (Fig. 1) and granitic rocks (Fig. 10) become diffuse and possibly blend into each other in just the composition range of andesites and diorites.

Rhyolites are considered under granitic rocks, but it may be that a more extensive study of the trace elements of rhyolites will establish a difference of origin for different rhyolites (e.g. result of magmatic differentiation or fusion of subsurface sediments).

Strontium in Basaltic Rocks

Rocks under the general classification of basaltic rocks as well as andesites and anorthosites are included in this section. Differences between the extremes of composition showed little effect on the strontium distribution. The present study shows that no measurable difference between extrusive and intrusive equivalents exists as far as strontium is concerned. Also included in this section are certain altered basaltic rocks such as spilites and metabasalts.

Pattern of Distribution

One of the major concepts of the geochemistry of trace elements as enunciated formally by Goldschmidt (1954) is that there is the tendency for certain minor elements to follow major elements that are similar to them in radius and bond type. The degree of this coherence has been an object of study by many investigators. From these studies there emerges the fact that there are at least two levels of geochemical coherence.

On the most general level, certain minor elements will substitute quantitatively for one or more major rock forming elements in preference to others, e.g. thallium in potassic minerals. Strontium follows this rule, and is usually found in the calcium-rich minerals and to an equal or lesser extent in high-temperature potassium minerals.

A higher level of coherence is illustrated by several pairs of elements such as K—Rb, and Zr—Hf. One element forms a common silicate mineral, while the other is much less abundant and consequently does not. It has been shown that at least in the case of such element pairs there is a marked covariance of the concentration of these elements for nearly all types of earth conditions. As the concentration of the major element increases in a particular phase, so does the concentration of the geochemically coherent minor element.

The relations of strontium and calcium in basaltic rocks indicate that, though

the general level of coherence may be attained to some degree, there is no marked universal covariance of strontium and calcium. This is best seen in Fig. 1, where a plot of log strontium vs. log calcium shows clearly that, within limits, any value of strontium is possible for a given calcium content. This is undoubtedly due to the regional differences in strontium content of the source magma and, locally, fractional crystallization and differentiation. It is evident that the strontium content of basaltic rocks is dominated more by these two factors than coherence with calcium.

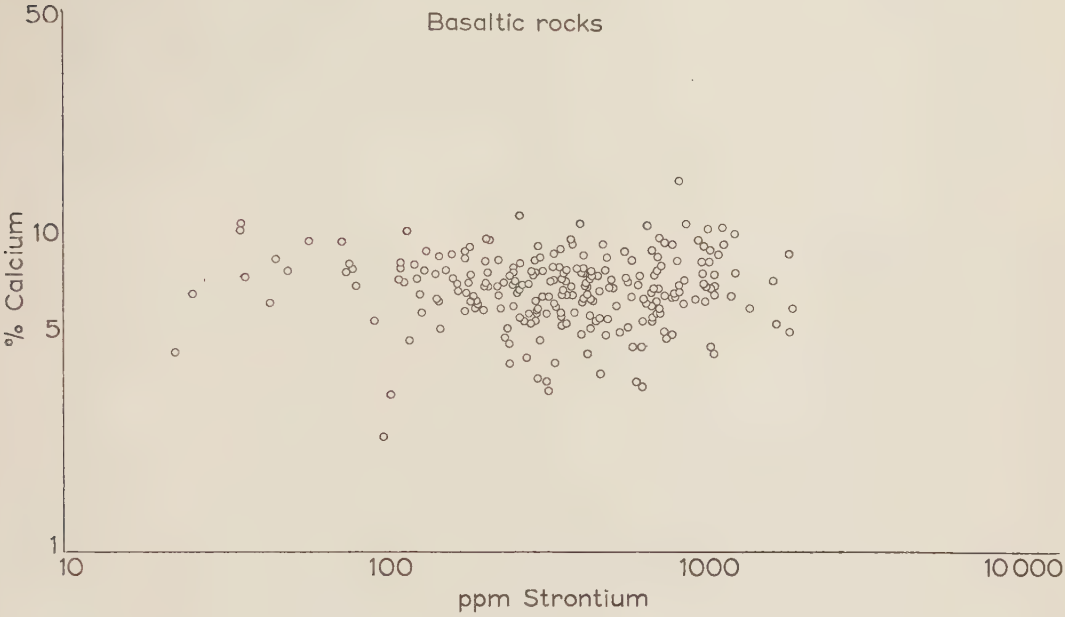

Fig. 1. Plot of log Ca against log Sr for 245 basaltic rocks.

It will be seen that in the case of granitic rocks the effect of geochemical coherence of strontium with calcium far outweighs the effects of regional variations.

If the logarithms of the strontium content of all the basaltic rocks are plotted as a histogram, it is seen that a very close approximation to a normal distribution results (Fig. 2). The large number of samples make it likely that in the case of basaltic rocks lognormal distribution is a probable one.

It is not important to the present development if the distribution is precisely lognormal or not. The significant point is that when a logarithmic transformation is made of the variate, a nonskewed distribution is evident for basalts, whereas a similar operation in the case of granites (see below) yields a skewed histogram. The exact meaning of lognormality must be deferred until the causal relations are better understood.

Estimation of the Crustal Abundance of Strontium in Basaltic Rocks

As most of the basaltic rocks are present on the surface of the earth, either in the oceanic crust or as flows and sills, it is difficult to make an estimation of the

crustal abundance by taking the value for a particular area and weighting it by the total volume of the rock of that area. Additionally, there is no conclusive answer to how much basalt has been eroded during geologic time from different areas.

The only method then that appears to have merit is to estimate the abundance of strontium by considering the simple arithmetic average. Though there always is the possibility of being in error in such a technique due to sampling bias, there are several clues which tend to give confidence to the present estimate.

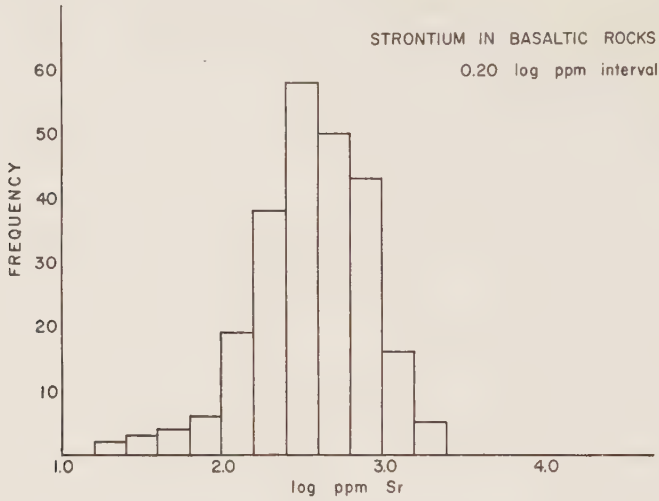

Fig. 2. Histogram of strontium in basaltic rocks with a logarithmic transformation of the variate.

First, because strontium is not geochemically coherent with calcium (or any element), as was seen above, the sampling is bound to be more truly random than in the case of granitic rocks, where coherence is marked.

Second, it is seen that a regular distribution is obtained when a logarithmic

Table 5. Comparison of the present estimate of the abundance of strontium in basaltic rocks with those of previous investigators

Investigator or Compiler	p.p.m. Sr
Noll (1934)—compilation of literature (mainly chemical analyses)	170
Hevesy and Würstlin (1934)	140
Sahama (1945) Southern Lapland	80
Present average	465

plot is made (see below) of the strontium content in a histogram. This also tends to give confidence in the randomness of the sampling (AHRENS, 1953, 1954b), although it certainly is not a conclusive proof.

Finally, if two methods of averaging are compared, they are almost identical.

(1) From the average of 244 basaltic rocks (including basaltic andesite and anorthosites) a simple arithmetic mean gives 467 p.p.m.

(2) By taking the average of each of 25 areas and assuming that each was equally probable (irrespective of the number of observations in each area), a value of 462 p.p.m. is obtained.

Hence, it can be estimated that the crustal abundance of strontium in basaltic rocks is probably close to 465 p.p.m. This is considerably higher than most previous estimates (Table 5). This discrepancy can be attributed to limited or local sampling by the earlier investigators or analytical errors, as discussed above.

Discussion of Basalt Analyses from Various Regions

From the analysis of the data on basaltic rocks, three relationships present themselves: (1) The dispersion in strontium values for most provinces, where defined, is small. (2) There are marked differences between the means of different

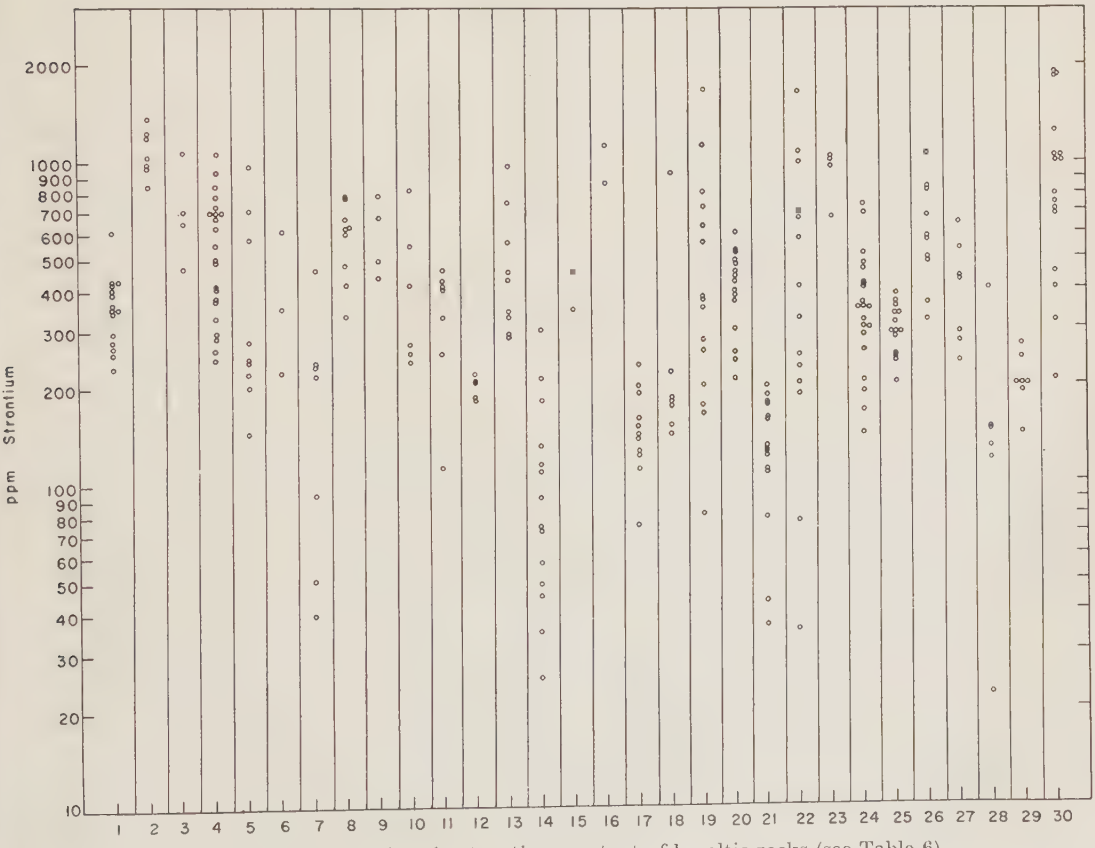

Fig. 3. Regional variations in strontium content of basaltic rocks (see Table 6).

Table 6. Regional variations in strontium content of basaltic rocks

Number in figure	Region	Number of samples	Avg. p.p.m. Sr
	Oceanic Islands		
1	"Primitive" Hawaiian Lavas	15	385
2	"Late Stage" Hawaiian Lavas	7	1091
	Avg. of Hawaiian Lavas	22	594
3	Atlantic Islands	4	730
4	Intra-Pacific Islands (excluding Hawaii)	21	554
5	Japan	9	400
6	Aleutians	3	397
	Europe		
7	Switzerland (Spilitic Basalts)	7	192
8	Turkey (Tertiary)	9	593
9	Finnish Pre-Cambrian	4	594
10	Great Britain	6	427
	India		
11	Archaean Basalts	7	344
12	Mesozoic (including Deccan)	5	198
	Africa		
13	Karroo Basalts	9	491
14	Archaean Metabasalts (mainly Bulawayan)	15	107
15	Deweras System	2	402
16	Lake Kivu Area	2	990
17	Lebombo Volcanics	11	150
	South America		
18	Venezuela (excluding Amazon Basin)	6	176
19	Brazil	15	520
	North America		
20	North Carolina Metabasalts	15	407
21	Eastern U.S. Triassic	15	129
22	Eastern U.S. Pre-Triassic (excluding Adirondacks and North Carolina)	14	524
23	Adirondacks	4	919
24	Middlewestern and Canadian Pre-Cambrian	21	369
25	Pacific Northwest "Tholeiitic Basalts"	14	299
26	Pacific Northwest "Olivine Basalts"	10	620
27	Pacific Northwest "Clarno Fm."	7	407
28	Beartooth Plateau, Montana Basaltic Dikes	6	160
29	Stillwater Complex plagioclases, Montana	7	206
30	Western North America	16	943

provinces. (3) Some basaltic rocks show the effect of magmatic differentiation and others do not.

The regional discussion below serves mainly to emphasize these points, and is not to be considered a detailed petrologic analysis of any basaltic region. It does show the usefulness as well as the limitations of applying quantitative trace-element analysis to problems of petrogenesis. In presenting a more or less systematic review of the strontium data for each area, it is hoped that the following discussion will serve as an aid to petrologists familiar with these regions or others with similar problems. In that sense it is proposed that it be used more in the nature of a reconnaissance study than as a final statement.

The data for all the areas have been plotted in Fig. 3. Table 6 lists the various arithmetic averages for each area.

Stillwater complex. The Stillwater complex is a mafic magmatic differentiate of Pre-Cambrian age in southwestern Montana. Only the lower portion of the differentiated pluton is available for study, the upper portion having been eroded. The analyses were made on plagioclase crystals separated from the anorthosites and gabbros of the area by Professor H. H. Hess.

From the lower to the upper part of the complex the plagioclase composition ranges from An_{86} to An_{62}. There is a steady decrease in calcium content, with some minor variations. Table 7 lists the plagioclases. It is seen that with a decreasing calcium content there is an increase

Table 7. Strontium and calcium content of plagioclases from the Stillwater complex, Montana

Sample No.	mol. %An.	%Ca	p.p.m. Sr	$\frac{\%Sr}{\%Ca} \times 10^3$
HM 5	86·1	12·4	141	1·14
HM 1	80·3	11·6	191	1·65
HM 8	79·6	11·5	196	1·70
HM 10	79·1	11·4	200	1·76
HM 9	75·4	10·9	201	1·84
HM 2	74·5	10·7	243	2·27
HM 3	62·5	9·0	270	3·00

in the strontium content of the plagioclases. The strontium is preferentially left in the residual magma, thus increasing the Sr/Ca ratio in the liquid. As crystals form with progressively lower temperature and lower calcium concentration, they will show an increase in the Sr/Ca ratio in the lattice. The last crystal formed would have the highest Sr/Ca ratio, and the lowest content of Ca.

Fig. 4 illustrates the negative slope when the Sr/Ca ratio is plotted against increasing calcium content. Wager and Mitchell (1951) have pointed out the same situation for the Skaergaard complex of Greenland.

Oceanic Islands

The islands of the Pacific are regarded by many petrologists as being of the same petrographic clan and presumably of the same origin. There are variations in lithology both within the petrologic suite of one group of islands and between groups, but generally these differences have been considered relatively minor compared to the similarities. The Hawaiian group perhaps has been the most intensively studied of all, and there is an indication that the origin of the basaltic series, if understood for this group, may provide the explanation for the rest.

One of the latest surveys of the petrogenetic problem of the Hawaiian rocks has been made by Powers (1954), who accepts the idea that the alkali rocks found on the surface of many of the Hawaiian Islands may not be truly representative of the main magma composition. The true "primitive" magma is to be found in the presently active volcanoes such as Mauna Loa and Kilauea. If the strontium value of these "primitive" rocks (mainly basalts, more or less olivine-bearing) are compared with the strontium value of rocks formed in the late stage of volcanism, a marked difference is seen (Fig. 3). When a plot of the $\%Sr/\%Ca \times 10^3$ is made

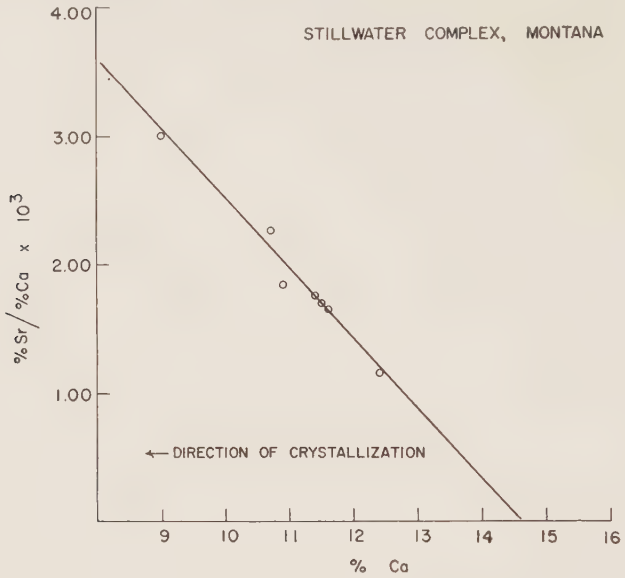

Fig. 4. The relation between Sr/Ca ratio and magmatic differentiation in the Stillwater complex, Montana.

against the per cent of calcium in the rock (Fig. 5), a rough negative slope is seen for the late-stage rocks, thus indicating possibly the same type of magmatic differentiation as was observed in the Stillwater complex.

This is in accord with the idea of several geologists that the primitive basalt is made by fusion of the pyroxene and plagioclase component from the subcrustal peridotite, followed by rapid and forceful ejection of this lava because of the high volatile content. As either the energy or the material for such activity is diminished, and as the volatile content decreases, the rising lava becomes sluggish and tends to remain in a subterranean magma chamber, where fractional crystallization and settling, possibly with assimilation, give rise to the late-stage magma series. This is borne out by the strontium data.

The agreement between the mean for the primitive basalts of the Hawaiian rocks (398 p.p.m.) and geometric mean of all the basaltic rocks (340 p.p.m.) may be only fortuitous or it may indicate that the Hawaiian composition is the most probable composition for most basalts derived from the mantle and that any diminution or increase is due to mixing with continental rocks of low strontium content in the former case and magmatic differentiation in the latter.

The mean of all the rocks of Hawaii compares with the mean of all the other rocks of the Intra-Pacific region (Table 6). The lack of any pattern for the groups is probably due to the limited sampling control. Most of the analyses are on Lacroix's classic collection. The high value of strontium may mean that too much emphasis was placed on the late-stage rocks (which would tend to be surficial).

The averages for the Japanese islands and the Aleutians are almost identical (Table 6). Further, they agree with the value of the primitive Hawaiian basalts.

The average strontium concentration of basalts from the islands of the Atlantic and Indian ocean, based on four samples, is higher (730 p.p.m.) than the intra-Pacific islands (554 p.p.m.), but this is probably not significantly different. After testing if there was any significance in the variance of the two suites of analyses (with negative result), the test for the significance of a difference in the means was performed. Neither the regular analysis nor the analysis where a logarithmic transformation was made showed the difference to be significant.

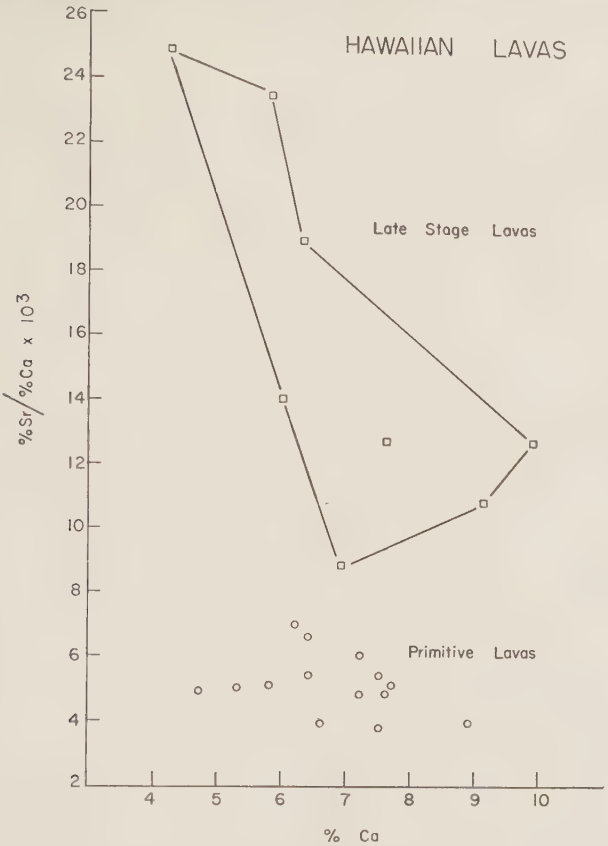

Fig. 5. The relation between strontium and calcium for Hawaiian "Primitive" lavas and "Late Stage" lavas.

European Basaltic Rocks

Table 1 shows the values for calcium and strontium for seven spilites from Switzerland. There is a very wide range in the strontium content for the spilitic rocks, and there is no correlation with the calcium content. In large basaltic provinces the basaltic rocks appear either very uniform or, where fractional crystallization occurs, show a definite trend in the direction of an increase in the Sr/Ca ratio with decrease in the calcium content. The spilites do not show either pattern, indicating an unusual history. The possibility of metasomatic transformations as the basalt interacted with either water-soaked sediments or the sea itself has been suggested for the origin of the spilites. The present data would tend to add one more confirmation of a unique origin for these rocks associated with orogenic areas.

The Oslo Region rocks are an alkalic complex related to a rather extensive Permian fissure zone which has been traced all the way to southern France. The region has been under intensive study by Norwegian geologists ever since Brögger (1933) made his first classic studies. The

discussion of the Oslo Region has been put under the section of basaltic rocks more for the sake of convenience than any genetic relationship. However, approximately half of the rocks analysed from this region are members of the basaltic clan, in the broad sense used in this paper. It has been recognized, nevertheless, that the amount of mafic rocks is quite small relative to the great abundance of rocks of an alkalic affinity. It has been stated (Goldschmidt, 1954; Noll, 1934) that alkalic rocks are generally higher in strontium than granitic or basaltic rocks. It can be seen that, at least in the case of the Oslo rocks, this generalization is not warranted.

Two foyaites (JD 3 and JD 9) are represented from this same area. Their origin may not be the same, but it will be noted that, though both have the same calcium content, JD 3 has 1467 p.p.m. strontium, whereas JD 9 has 62 p.p.m.

The dominant members of the alkalic series are thought to be the result of crystallization-differentiation of a syenite magma. Whether this conclusion of Barth's (1954) is the only possible mode of genesis must remain for the solution by petrologists. However, some light may be thrown on the problem of petrogenesis by the Sr-Ca relationships observed.

According to Barth (and others), the direction of crystallization is:

Kjelsåsite → Larvikite → Nordmarkite → Ekerite

This is in the direction of a more silica-rich rock. The alkali content is approximately constant. However, there is a marked decrease in calcium content from left to right. This is seen in the mineralogy, since the plagioclase changes from andesine in Kjelsåsite through oligoclase for Larvikite to the alkali feldspars for the last two members.

The relation between strontium and calcium in this series (Fig. 6) is similar to that observed for granites (see below) and not that for magmatic differentiates of the Stillwater or Skaergaard type. One explanation of this observation is that the normal crystallization of a magma is such as to give a negative slope for the Sr-Ca relationship for the early segregates (as the Stillwater Complex) and a positive slope for the late segregates (as in the case of the Oslo Rocks).

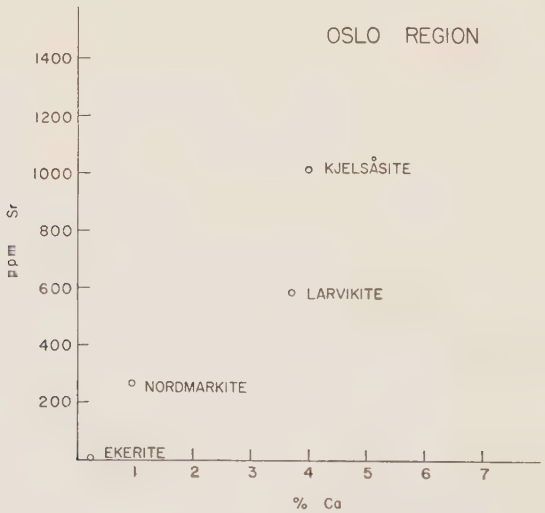

Fig. 6. Relation between strontium and calcium for some rocks of the Oslo region, Norway.

A second possibility is that the Oslo Rocks have either been subject to metamorphism resulting in the destruction of the original differentiation distribution of strontium, or that the Oslo rocks themselves are primarily metamorphic in origin rather than simple crystallization-differentiation.

A series of nine analyses of Turkish basaltic rocks presumably of Tertiary age shows a rather uniform and high value of strontium (593 p.p.m.).

Four analyses of Finnish Pre-Cambrian basaltic rocks give a value of 594 p.p.m. strontium, with a small dispersion around this mean value.

The samples of basaltic rocks from Great Britain are mainly from the Irish and Scottish Tertiary Province associated with the flood basalts extending to Iceland. They give a value of 427 p.p.m. When this is compared with a value of 730 p.p.m. for the Atlantic Islands, it is seen that a difference occurs, since with the application of the t test a significance level of between 2·5% and 5% is attained. This tends to confirm the idea that the source of the Brito-Arctic region flood basalts is different from the Atlantic Ridge-associated rocks.

India

There is a difference between the metabasaltic rocks of Archaean age of India and the Mesozoic basalts (including the famous Deccan traps). The Archaean basalts have 344 p.p.m. and Mesozoic basalts 198 p.p.m. of strontium. It must not be concluded that there is any universal significance to this variation with age, since in the African basaltic rocks the inverse relationship is evident.

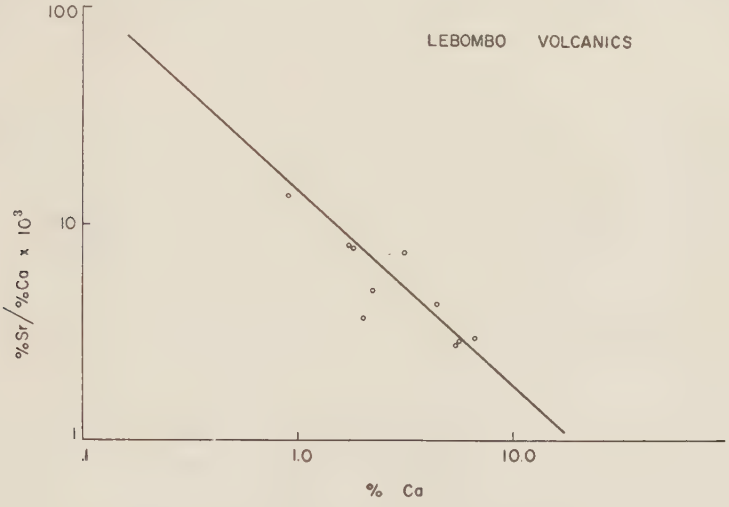

Fig. 7. Relation between strontium and calcium for the Lebombo volcanics, Swaziland.

Africa

The rift valleys of Eastern Africa include a wide variety of volcanics which have been produced intermittently since the Pliocene. These rocks are characterized by high potassium content. The Lake Kivu specimens are from the western rift associated with the Bufumbira potassic volcanic province, though the samples are probably olivine basalts. The strontium content is 990 p.p.m. Holmes and Harwood (1932) have also reported high values for strontium and barium for this region.

The Lebombo volcanics occurring in the eastern part of Africa (the samples are all from Swaziland) are probably late Triassic in age and represent a wide variety of chemical composition, as is seen in Table 1. If the rhyolitic members are the latest evolved, it means that as the magma was crystallizing below the surface there was a "ladling" off of the remaining melt, which with time became higher in the Sr/Ca ratio and lower in calcium content (Fig. 7).

The Karroo basaltic rocks are supposed to be typical tholeiitic flood basalts of Jurassic age, and extend a great distance in Southern Africa.

It will be seen that the average value of 491 p.p.m. strontium differs significantly from that of the early Pre-Cambrian system (107 p.p.m.).

As in the case of both the Triassic basalts of the eastern United States and the Mesozoic

basalts of India, the Karroo-system basalts show no differentiation trend as far as strontium is concerned. This may mean that these "plateau" basalts were derived quickly from the subcrust. There was no time for intratelluric fractional crystallization. The only fractional crystallization, if any, occurred in individual flows and sills once the magma had been emplaced. It will be seen that this is different from the tholeiites of the Pacific Northwest.

South America

A total of seven samples of basaltic rock were analysed from a wide area in Venezuela. Most of the strontium values were low. The average concentration of 176 p.p.m. strontium shows a very small standard deviation. One sample, however, from the Amazon area is 920 p.p.m. (AD 3), and another from the same area analysed qualitatively showed a comparable high value. Hence, these last two apparently represent a different geologic province. It has been shown that generally the spread in values of strontium for a well-defined geologic system is quite small relative to variations between areas with a few exceptions, such as the Swiss spilites.

The samples from Brazil are from many different geologic systems, hence the spread in values from 80 p.p.m. to 1671 p.p.m. strontium. It would be possible to say more about the significance of these numbers if a better control in the age and association of these samples were known.

North America

The samples from the Bakersville-Roan Mountain Area include three suites of amphibolites. The first group represented by samples MD 1–MD 7 (see Table 2) are known to be metadiabases related to the Bakersville dike swarm (Wilcox, 1955) cutting the Cranberry gneiss of that region. Overlying the Cranberry is the Roan formation, where the amphibolites have been found mainly to be of sedimentary origin. These are represented by samples BK 303–310. The third suite of samples (MD 8–MD 15) represents amphibolites of uncertain origin found near the Roan-Cranberry contact at the edge of Bakersville dike swarm. A semiquantitative analysis for Ga, Ba, Ni, Co, and Cr in these various amphibolites showed that, on the level of information obtained, the metadiabase of the Cranberry and the para-amphibolites of the Roan could not be distinguished from each other, thus not resolving the problem of the origin of the amphibolites in question.

However, the strontium values tell another story, since the metadiabases of the Cranberry have an average of 326 p.p.m. strontium, whereas the Roan para-amphibolites have 144 p.p.m.

The present study also shows that there is a significant difference between the means of the strontium contents of the Bakersville amphibolites (metadiabases) and the amphibolites of the Roan near the Bakersville dike swarm. The former has an average of 326 p.p.m. strontium, while the latter has 478 p.p.m. The application of the t test yielded a high probability of the significance of the difference between the two suites.

Hence, the following comparison is possible:

	avg. p.p.m. Sr
Bakersville dike swarm metadiabase	326
Roan para-amphibolites	144
Border amphibolites (uncertain origin)	478

From these data it is not possible to relate unequivocally the border amphibolites to either of the major groups of known origin. It has been suggested by R. E. Wilcox, on field evidence (personal communication), that the border amphibolites might be of a unique origin not related to either of the other metamorphic suites.

During late Triassic time a series of basaltic flows and sills was formed along the eastern sea-coast in a structural and stratigraphic basin called a "taphrogeosyncline" (Kay, 1951). This taphrogeosyncline extended from South Carolina to Nova Scotia, though at present not continuously outcropping along the strike. It is of considerable importance then that the strontium content for this series is not only low (129 p.p.m.), but highly uniform along the strike. Further, there is no evidence of fractionation among the various units, though fractionation within a single unit does exist (e.g. the Palisades sill, Walker, 1940). This is in accord with

what was found in other areas prominent for flood basalts, like the Deccan of India and the Karroo of South Africa. The tholeiitic basalts of the Columbia River Plateau do show fractionation, however, and hence, though macroscopically similar, there may be a difference in petrogenesis.

The pre-Triassic basaltic rocks of the Eastern United States include a wide variety of rocks of different ages, and undoubtedly for this reason give a very wide dispersion. Better controls would have been desirable, but even so it is clear that most of the values are much higher than the Triassic lavas (the two exceptions are from the Maryland-Delaware region and may be unusual in origin). The average value is 524 p.p.m.

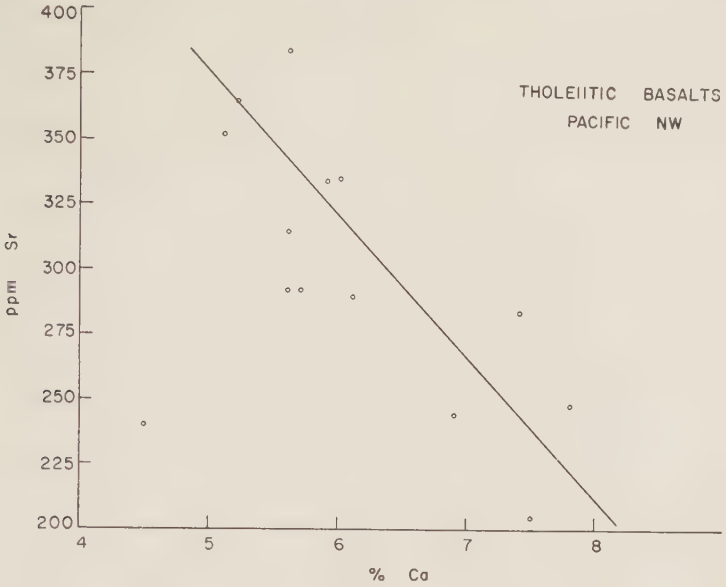

Fig. 8. The relation between strontium and calcium for the tholeiitic basalts of the Pacific Northwest.

There are four samples associated with the Adirondack basic batholith, and these all show a high consistent value for strontium (average is 919 p.p.m.).

The Keweenawan rocks of the Lake Superior Region show a moderate variation of strontium content around a mean of 369 p.p.m. This is markedly higher than the single analysis for a Keewatin age basalt, which gave 98 p.p.m. strontium.

In the Rocky Mountains and the Basin-Range Province there are widespread Tertiary basaltic and andesitic flows extending from Utah, Nevada, Colorado, Arizona, to Mexico. The wide dispersion may be attributed to variable contamination and differentiation. The average value of 943 p.p.m. reflects the high concentration of strontium in these rocks.

There are three sequences of basaltic rocks, according to Waters (1955), that are generally lumped indiscriminately as the Columbia River Plateau basalts. The oldest series, of Eocene age, is represented in these analyses by the Clarno formation suite. These are mainly andesites and basalts. They show an average composition of 407 p.p.m. strontium, a rather wide dispersion (relative to the other two suites), and show no correlation of the strontium and calcium contents.

The true Columbia River Basalts are the tholeiitic basalts of Miocene Age. These rocks are represented by thousands of feet of rather thin flows which may or may not show differentiation within flows, but generally are monotonously similar to the naked eye and microscopically. A plot of the strontium content against the calcium content, however (Fig. 8), shows a definite trend with a negative slope. This negative slope is interpreted, from the information available of the magmatic differentiates of the Stillwater and the Skaergaard complexes, as the consequence of fractional crystallization.

The question arises at this point: were the tholeiitic flows derived from a process of "ladling" off of a magma undergoing crystal differentiation, or can this same effect be due to an alternative process of gradually re-fusing a large body of previously differentiated rock where each succeeding flow will represent a higher temperature of fusion? If the latter is the case, then the stratigraphically lowest flows would be expected to be higher in strontium and lower in calcium than the later flows. Two cases were tested for this (Table 8), and there is a definite lower strontium value for the later flow, thus indicating that the second hypothesis may very well be true. It means then that the Miocene tholeiitic flows are somehow different from the other plateau basalts studied. They may represent the gradual fusion with increasing heat of a differentiated body or possibly even a solidified homogeneous mass in the subcrust.

The true olivine basalts (Waters) of Pliocene to Recent age show a higher average value of strontium (620 p.p.m.), with a somewhat larger dispersion than the Miocene tholeiites. They show no correlation of strontium with calcium, hence are probably of different origin. In this respect they are similar to the olivine basalts of Hawaii (except for the higher mean value of strontium content).

Table 8. The stratigraphic variations of Sr and Ca content of Pacific Northwest tholeiitic basalts

Sample	Stratigraphic Description	%Ca	p.p.m. Sr
	Crescent Bar, nr. Trinidad, Washington		
QD 3	2nd flow from top of section	6·9	244
QD 4	10th flow from top of section	6·1	290
	Roza Gap, N. of Yakima, Washington		
QD 5	1st flow from top of section	7·5	204
QD 6	8th flow from top of section	5·9	335

Strontium in Granitic Rocks

All specimens having a general granitic composition will be included in this section, regardless of apparent origin. Thus ortho- and para-gneisses, granodiorites, and other rocks of a sialic nature are considered here. The results discussed below show that, whether these rocks are of metasomatic or magmatic origin, a common pattern of distribution of strontium is present. The extrusive equivalents, approaching rhyolite, show a marked difference from their "plutonic" analogs.

Pattern of Distribution

The unique relationship of Ca and Sr in granitic rock can best be shown by an example from a single batholith, i.e. the Saanich granodiorite, a facies of the Coast Range batholith in southern Vancouver Island, B.C. Fig. 9 shows a plot of strontium content against calcium content for different rocks from this single body. It is evident that a positive slope results, i.e. the strontium content increases as the calcium content increases. This is opposite to the differentiation series of such basaltic bodies as the Stillwater complex and indicates a fundamental difference between these two dissimilar rock systems. The next step is to see if this relationship is retained throughout the crust or if regional variations in the strontium content will tend to overshadow this effect, as in the case of basaltic rocks.

The most instructive plot of the strontium and calcium data is shown in

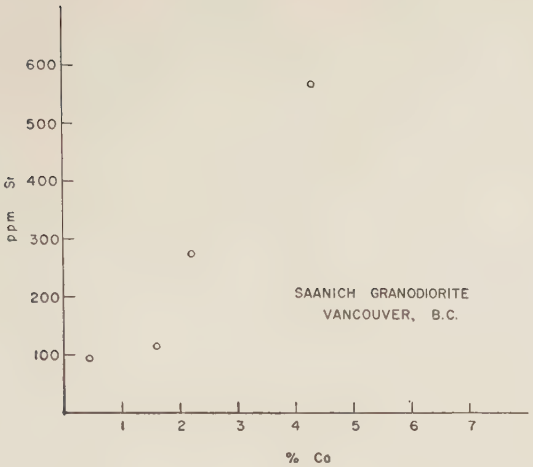

Fig. 9. The relation between strontium and calcium in the Saanich Granodiorite, Vancouver, B.C.

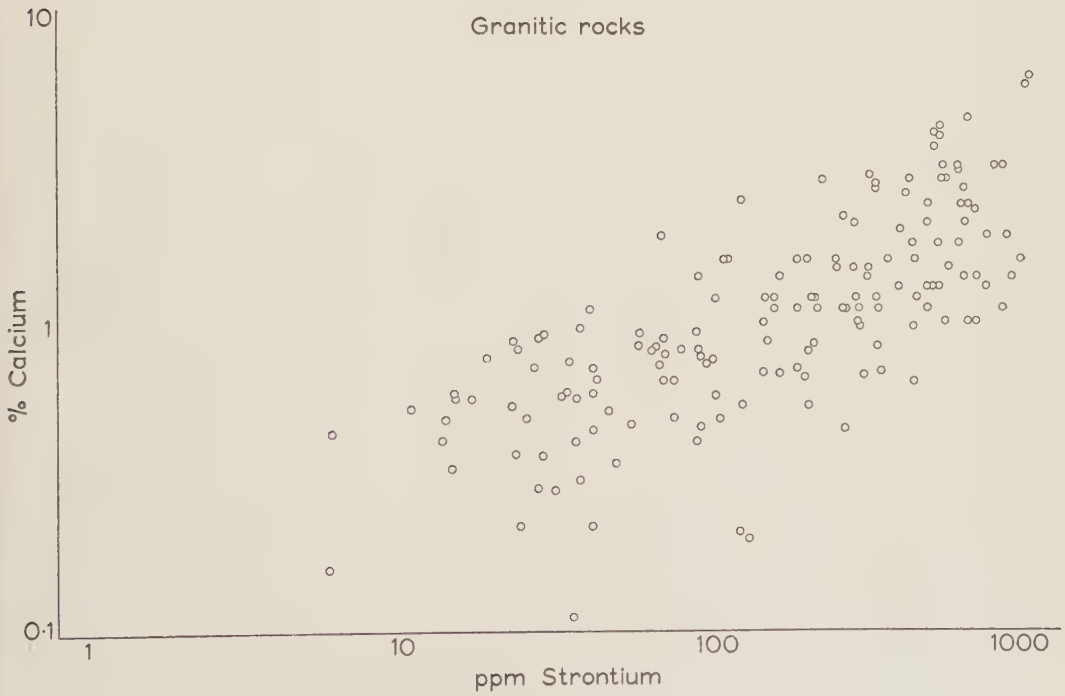

Fig. 10. Plot of log Ca against log Sr for 170 granitic rocks.

Fig. 12, where log Sr is plotted against log Ca. It is seen that a definite correlation exists viz. the strontium content of granitic rocks increases with the calcium content. It is evident then that, in the case of granitic rocks, those with higher calcium content will have a higher strontium content than those with lower calcium content but not in a simple linear relationship. The fact that such a coherence exists for granitic rocks and not in basaltic rocks must be accounted for.

If selectivity occurred during crystallization, either a negative or zero slope would occur, based on the data from basaltic and other differentiation series (see the Stillwater complex or Columbia River basalts), instead of the positive slope actually observed. If it can be shown, however, that in a differentiating magma the strontium tends to follow the calcium closely for low calcium values, then it is conceivable that crystallization could account for a positive slope, as suggested in the discussion of the rocks of the Oslo region. A problem with this explanation is that unless there is a constant supply of strontium and calcium to the granitic magma to allow the crystallization process always to maintain the same ratio, wide variations of the Sr/Ca ratio for a particular calcium content might be expected from area to area. This is not observed to the extent that it obliterates the covariance relationship.

It was proposed earlier (Turekian, 1955b) that the relation of strontium content to calcium content in granitic rocks was due to the retention of a similar primary relation in sedimentary rocks, from which the granitic rocks are supposedly derived. It has become obvious that the strontium and calcium contents are related only in calcareous shales where the Sr/Ca ratio of the calcareous portion is approximately constant. Since this is the case for only restricted suites or for deep-sea sediments, it does not seem applicable generally to granites, consequently this hypothesis must be discarded.

It has been reported by Shaw (1954a) that there are no significant changes in the trace-element content of a pelitic sediment undergoing different degrees of metamorphism short of granitization. However, it is conceivable that during such an intense metamorphism and metasomatism required to produce granitic rocks a high degree of mobility is possible for strontium and calcium. During the reconstitution of the rock the amount of strontium in a particular environment will be dependent on the calcium content of that region. This will result in the coherence of strontium with calcium.

Normal or Lognormal Distribution

If histograms are constructed of the strontium content of 156 granitic rocks, it is seen that a linear plot gives a highly skewed distribution and the logarithmic plot gives an unsymmetrical distribution (Fig. 11). The reason is obvious—the histogram depends on the choice of samples. There were obviously more high-calcium (hence high-strontium) rocks analysed than low-calcium rocks. This is not necessarily representative of the crust of the earth when three dimensions are considered, thus having an uncertainty as to what to use as the average value of strontium in the crust.

It is impossible to make the assumption of lognormality and choose the relative

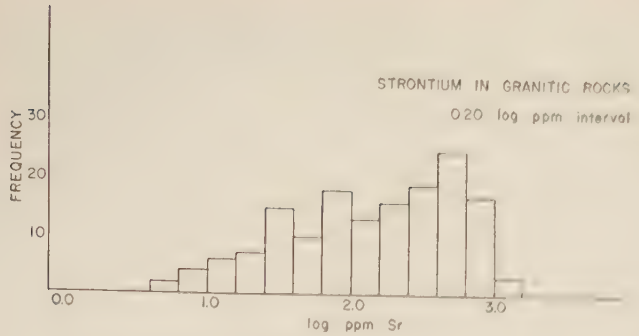

Fig. 11. Histogram of strontium in granitic rocks with a logarithmic transformation of the variate.

abundance of these rocks from such reasoning, since there is real doubt of the significance of such a plot (CHAYES, 1955; MILLER and GOLDBERG, 1955).

The Abundance of Strontium in Continental Rocks

In contrast to the basaltic rocks, which show no geochemical coherence (on the higher level) of strontium and calcium, the granitic rocks show the definite relationship discussed above. As this is the case, the problem of determining the abundance of strontium in continental-type rocks depends on the model of the composition of the crust chosen.

To illustrate this, a simple comparison will be made. If it is assumed that the continents are composed mainly of true low-calcium granitic rocks (in the strictest sense) and represent this by including all granitic type rocks having a calcium content up to 1·0%, it is found that the average of the corresponding strontium values is about 100 p.p.m. strontium.

On the other hand, if we assume that the continents are mainly composed of "granodioritic" composition and include under this all values of calcium from 1·0% to 5·0% calcium, a corresponding average strontium content of 440 p.p.m. is obtained. The average value for all "granitic" rocks comes to 285 p.p.m. Obviously, this latter figure is of doubtful significance, since it depends on how many high-calcium rocks were analysed relative to low-calcium rocks.

It is seen, therefore, that a wide range of strontium values can be obtained for continental rocks, depending on the range of granitic composition considered. If the rock distribution on the surface of the earth is considered to be representative of the distribution throughout the continental crust, and DALY's estimate (1933) of the crustal exposure of the various rock types in the United States is used, it is found that the low-strontium, low-calcium rocks (granites and rhyolites) occupy three times as much area in the United States as the granodiorites. Using the figures given above as an estimate of the strontium in each rock type, the granitic continental rocks turn out to have less than 260 p.p.m. strontium on the average.

On the other hand, if the model of the crust proposed by several modern geologists is taken (WORZEL and SHURBET, 1955; POLDERVAART, 1955), i.e. that the main part of the continents is composed of granodioritic material a value of

approximately 440 p.p.m. strontium is obtained. Implicit in the estimate of 440 p.p.m. for the continents is that the granodiorites of depth are similar in their Ca-Sr relation as the surficial rocks of the same type. This is a completely valid assumption, since many of the surface rocks are thought to have been at a considerable depth (up to 10 km) at some time in their history.

If present estimates are compared with past estimates, it is seen that there is a marked discrepancy. Generally, the past estimates have been too low. It is difficult to evaluate whether this was due to the selection of true low-calcium granites, insufficient sampling of the crust, or systematic errors in analysis. The estimates are presented in Table 9 together with values obtained here for the gross average of all granitic rocks, true low-calcium granites, and high-calcium granodiorites.

Table 9. Comparison of the present estimates of the abundance of strontium in granitic rocks with previous investigators

Investigator or compiler	p.p.m. Sr
Noll (1934) (compilation of data in literature, mainly wet-chemical analyses)	90
Hevesy and Würstlin (1934)	120
Present estimates	
All granitic rocks (170)	285
0·1–1·0% Ca—"granites" (85)	100
1·0–5·0% Ca—"granodiorites" (85)	440

Regional Variations

There are regional variations within the granitic clan just as there is for the basaltic one, but this depends on the prevalence of more or less calcium-rich rocks in the regions. The granitic rocks of New England, for example, are generally lower in calcium than the more granodioritic rocks of the Pacific Coast Range. Hence the former area has a lower regional strontium content than the latter. It was not always possible to relate ages with specific provinces, but where this could be done it is seen that there is no trend with age on a worldwide scale among the granitic rocks. From the foregoing discussion it is evident that the calcium content of a province of granitic rocks almost exclusively will determine the strontium content.

Figs. 12 through 17 show the distributions in six areas where large numbers of samples were available and fair control was present. The averages for each area are given in Table 10.

Rhyolites

If the strontium-calcium relationship in rhyolites is compared to the pattern for granites (Fig. 18), it is seen that half of the 20 rhyolites analysed fall outside the "main sequence," mainly in the direction of higher strontium for a given

calcium value. It must be noted that rhyolites appear to be both low in calcium and in strontium (Table 11), but that the Sr/Ca ratio is higher than the comparable granite (i.e. with the same calcium content).

Also from the plot of the log Ca versus log Sr it is seen that for all the rhyolites no distinctive pattern is discernible, as it is for the granites. In this latter respect they resemble the basaltic rocks, where the lack of correlation of Sr with Ca is

Table 10. Regional variations in strontium content of granite rocks

Province	p.p.m. Strontium
Canadian Shield	305
Rocky Mountains	328
New England	194
Western U.S.—Mesozoic	337
Fenno-Scandian Shield	246
Africa	160

the direct consequence of the abundance of Sr in the magma and not of any simple crystallographic response. The rhyolites then may represent the extrusion of granitic rock where the strontium content is a function only of the amount that is present in the magma. The conditions for attaining Sr/Ca ratio typical of granitic rocks of the same composition are not present.

Table 11. Comparison of strontium and calcium values for granites and rhyolites

	avg. %Ca	avg. p.p.m. Sr	$\frac{\%Sr}{\%Ca} \times 10^3$
Rhyolites: <1·0% Ca (20)	0·35	178	50·9
Rhyolites: all (23)	0·65	235	36·2
Granites: <1·0% Ca	0·6	100	16·7

Points falling below the "main sequence" of the log Ca versus log Sr plot are also of interest. They may best be explained as the consequence of magmatic differentiation. The strontium and calcium content of most pegmatites is generally very low, and yet the Sr/Ca ratio may be high (see the pegmatite from Finland, for example). Pegmatites are supposed to be the last differentiates of a fractional crystallization process. Likewise, if a subcrustal basaltic magma dissolved some of the surrounding granitic rock and then proceeded to differentiate, the last fluid crystallizing would probably be quite siliceous, and if extruded would form rhyolite with a low Ca and Sr content but a high Sr/Ca ratio. Another case is that of the Lebombo volcanics. Here it is seen that though there is not much change in the Sr content, there is a marked negative correlation of the Sr/Ca ratio with the

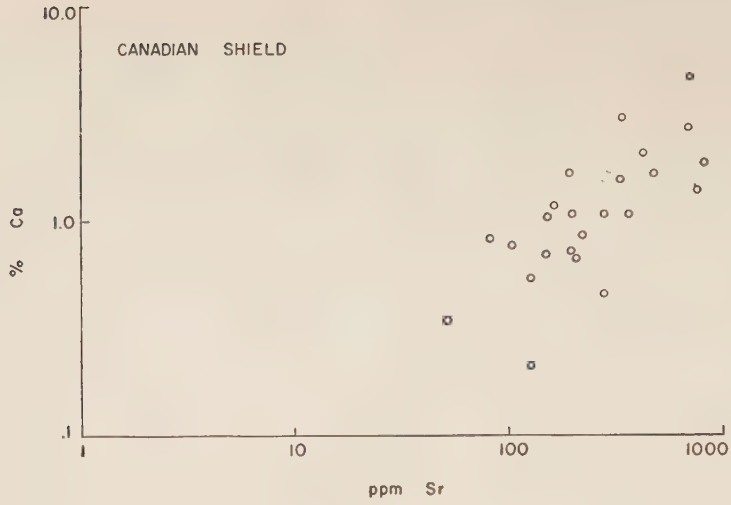

Fig. 12. Plot of log Ca against log Sr for granitic rocks of the Canadian Shield.

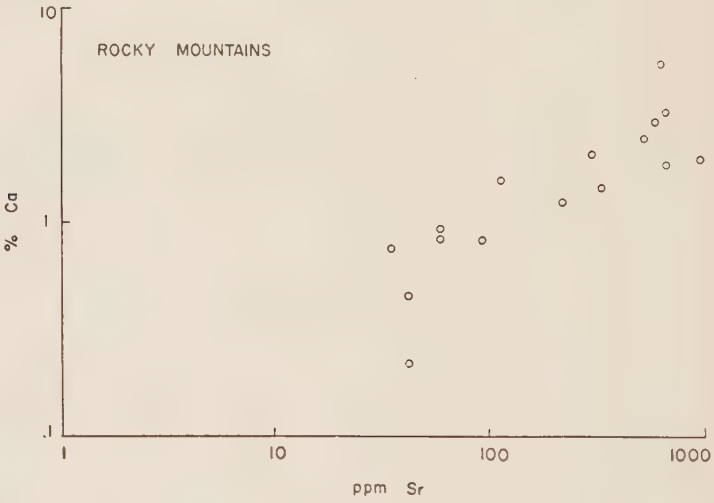

Fig. 13. Plot of log Ca against log Sr for granitic rocks of the Rocky Mountains..

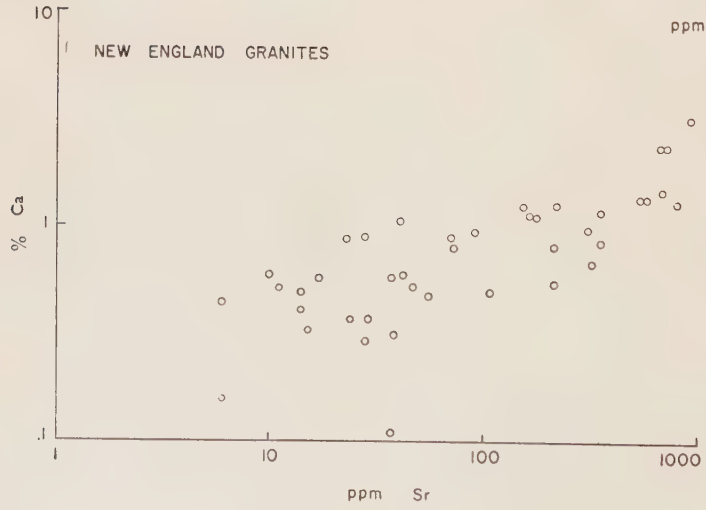

Fig. 14. Plot of log Ca against log Sr for granitic rocks of New England.

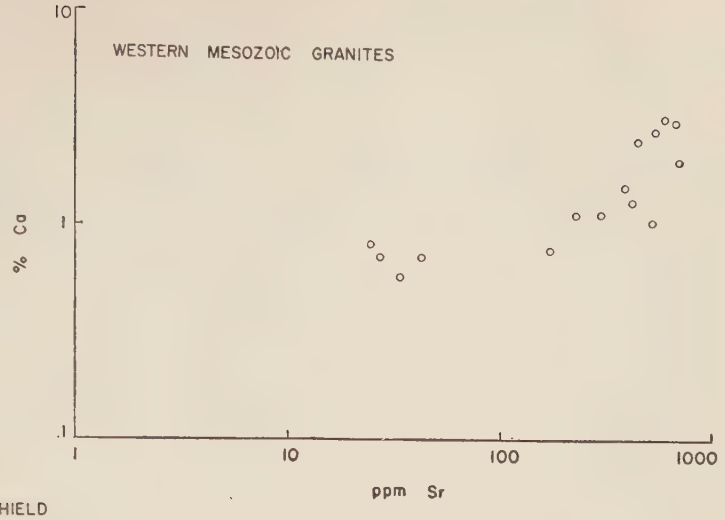

Fig. 15. Plot of log Ca against log Sr for granitic rocks of the Mesozoic of the Western United States.

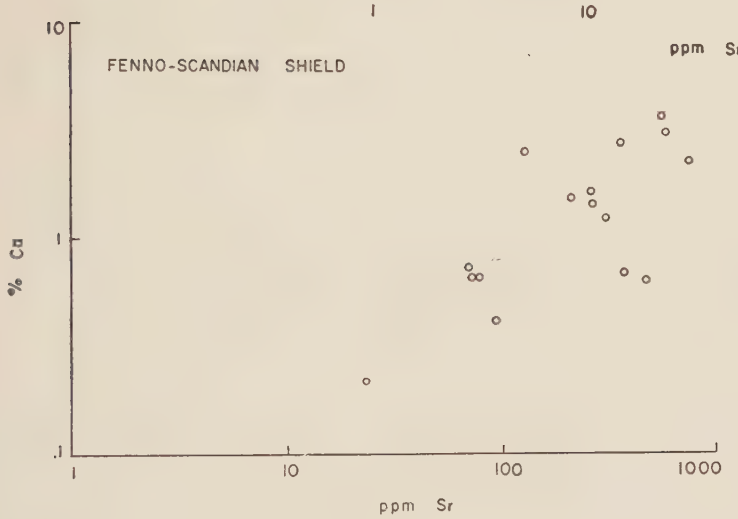

Fig. 16. Plot of log Ca against log Sr for granitic rocks from the Fenno-Scandian Shield.

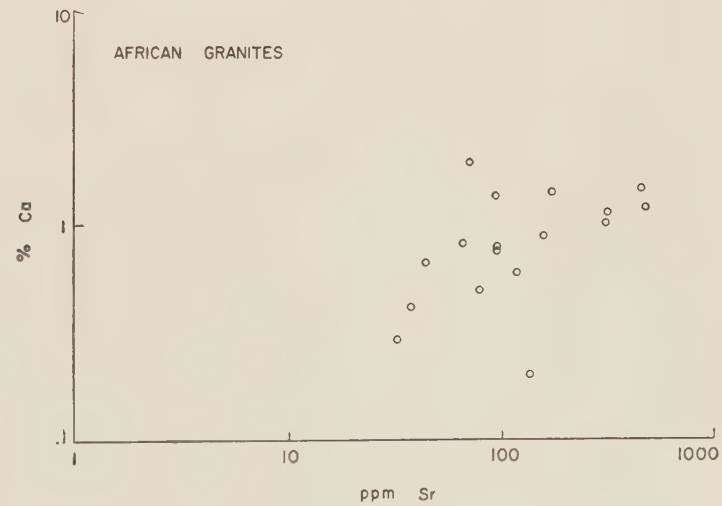

Fig. 17. Plot of log Ca against log Sr for granitic rocks from Africa.

calcium content of the flows (which range from rhyolites to basalts). See Fig. 8 and Table 1.

Sedimentary Rocks

The behaviour of strontium in sedimentary rocks is irregular because of the various influences of low-temperature deposition. Like calcium, its presence in arenites is quite limited. No sandstones or quartzites were analysed, but the level of strontium was found to be close to the detectable limit in several quartz samples. If quartz is representative of sandstone, then the strontium content of sandstone would probably not exceed about 20 p.p.m.

The behaviour of strontium relative to calcium in carbonate deposition, both organic and chemical, is a complicated story. Investigators realize that the ratio of strontium to calcium in carbonate shells and carbonate-bearing sediments is a function of several variables:

(1) The Sr/Ca ratio in the liquid phase from which the solid phase is derived;
(2) The particular polymorph—calcite or aragonite—into which the strontium is incorporated;
(3) The vital effect of the organism;
(4) The temperature;
(5) The salinity of the liquid phase.

In addition to the above primary effects, the sediment may be altered during diagenesis or by ground-water action. Variations in the strontium content of limestone and fossils have been discussed elsewhere considering the above complexities (Kulp, Turekian, and Boyd, 1952; Turekian, 1955a).

Shales

In shales the effect of the ion-exchange capacity of the clay minerals has a marked effect on the concentration of strontium relative to calcium, owing to the smaller ionic potential of strontium. Most shales, however, are not "pure" silicate shales, but contain more or less calcium carbonate, and the story is complicated by this fact.

As can be seen from Table 3, most of the shales examined are from the eastern United States. The reason for this sampling was the ready availability of these shale specimens. It is hoped that this situation will be improved in the future in a more extensive study of pelitic rocks for other trace elements as well as strontium.

The average value of the 69 shales analysed is 298 p.p.m. This is considerably lower than that given by Shaw (1954b), who reports a value of 700 p.p.m. On the other hand, Hevesy and Würstlin (1934) reports 20 p.p.m. for shales and phyllites, which is obviously too low.

The value of 300-p.p.m. Sr for shales is probably closest to the true abundance for this rock-type. Although most of the shales analysed are from the eastern United States, it is evident from the discussion in the next section and under schists that pelitic rocks generally have a constant value of strontium. The plot of log $\%Sr/\%Ca \times 10^3$ against log Ca for both the shales (mainly Palaeozoic rocks of the eastern U.S.) and schists (a wide variety of ages and locations) indicates that

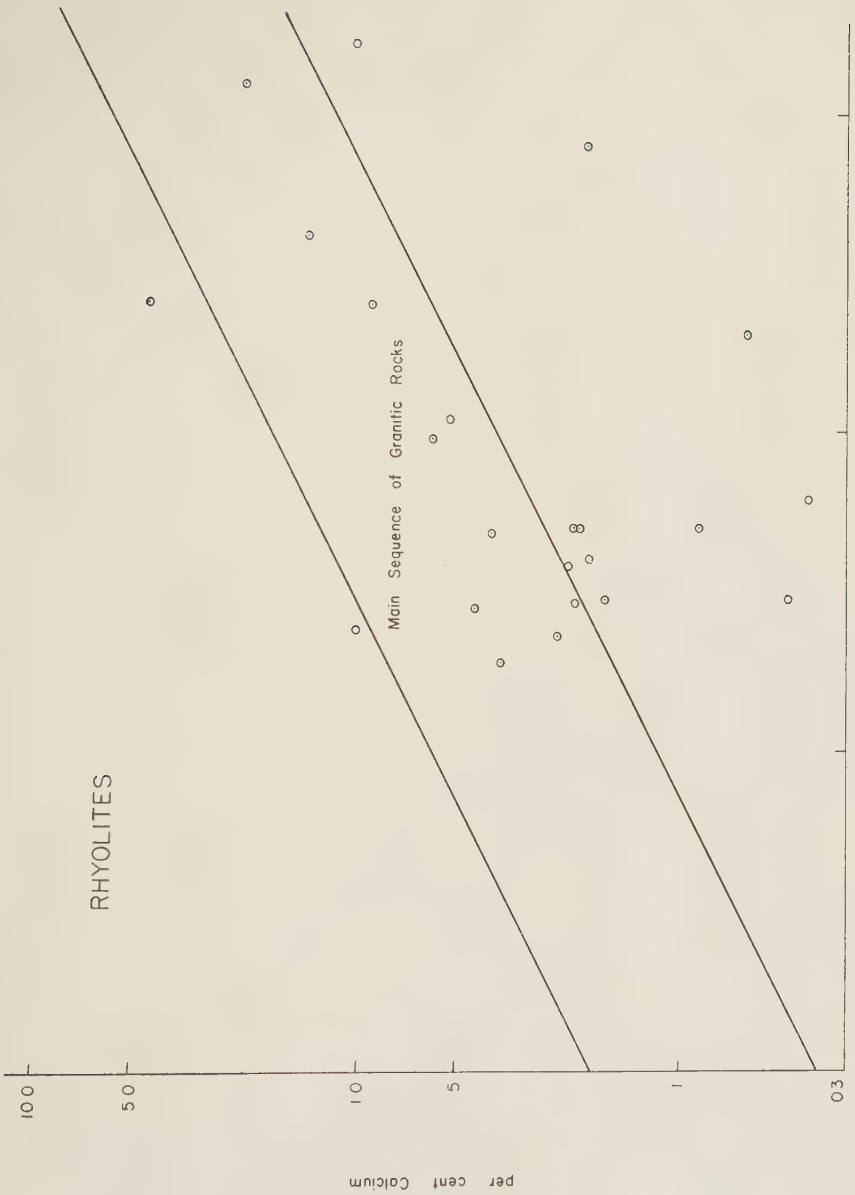

Fig. 18. The relationship of rhyolites to granites, as seen in the plot of log Ca against log Sr.

the two sets of points lie along the same line. This is also reflected, of course, in the similarity of the average values of strontium of the shales and of the schists.

The Pattern of Distribution

Odum (1950) made the observation that the Sr/Ca ratio increased with a decrease in the calcium content of pelitic rocks and sediments. If a plot of log

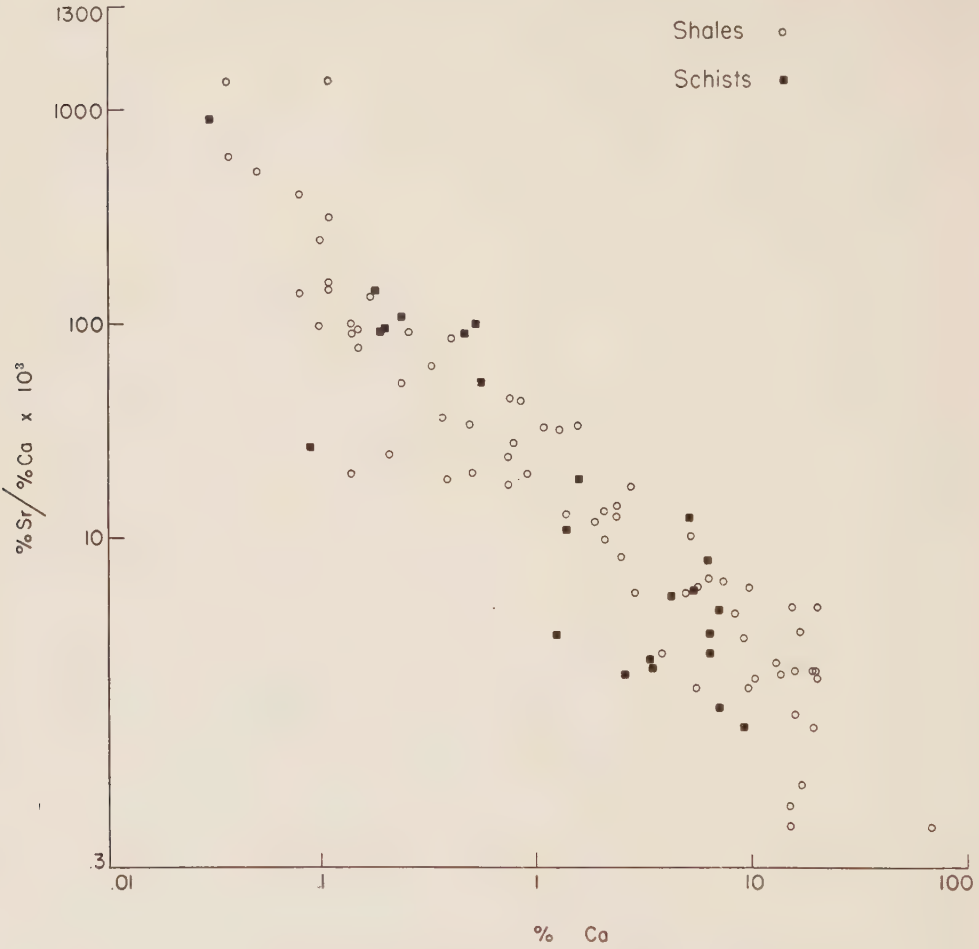

Fig. 19. Plot of log Sr/Ca against log Ca for shales and schists.

%Sr/%Ca versus log %Ca for this new data (Fig. 19) is made, a negative slope results, with an angle of about 45°. This means that the strontium content is independent of the calcium content. Such a result was not predictable, because strontium occurs in both the carbonate fraction (where undoubtedly most of the calcium occurs) and bound on the clay particles. Neither component has the ability of dominating the pattern of strontium distribution, and consequently this relationship must be considered wholly fortuitous. In this respect the random

selection of geosynclinal sediments shows a marked difference from the pelagic sediments of the deep sea.

If the 69 shales are used to make a histogram with the logarithm of the strontium content as the variate, there is a good symmetrical distribution (Fig. 20), as in the case of the basaltic rocks and limestones. The relation between this observation and the fact that the strontium content is independent of the calcium content is discussed later.

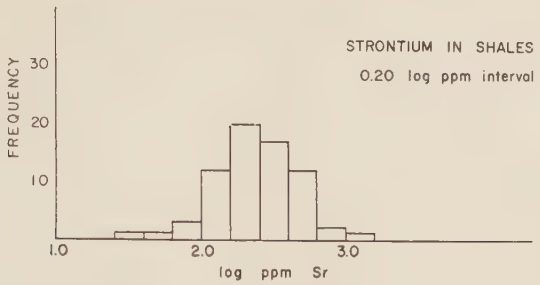

Fig. 20. Histogram of strontium in shales with a logarithmic transformation of the variate.

Variations with age. Table 12 and Fig. 21 show the variations in the strontium content of shales within and among geologic periods. The average values indicate different strontium content for different geologic ages in the eastern United States. The significance of the difference in the means was tested in the case of two samples, the Ordovician and Silurian, by an analysis of variance. Two analyses were carried out, one using the p.p.m. strontium data and the other using the logarithm

Table 12. Averages of strontium for shales of the United States of different ages

System	No. of observations	Average p.p.m. strontium
Cambrian	5	261
Ordovician	12	404
Silurian	10	316
Devonian	24	245
Mississippian	7	124
Pennsylvanian	7	430
Mesozoic	4	384

of p.p.m. strontium. It was observed that in both these cases the difference between the Ordovician and Silurian samples was possibly significant. (The F test on the variance between samples relative to the variance within samples showed that the variance ratio fell between the 5% and 10% F points.) This can be extended visually to the other samples and the conclusion drawn that the means between the samples may be significantly different.

If this is true, it is a matter of speculation as to the meaning of the variation.

One possibility is that sources containing different concentrations of strontium supplied the sediments through the Palaeozoic. Considering the development of the stratigraphy of the eastern United States, according to Kay (1951), this is not an unlikely proposal. However, more extensive studies must be made along this line.

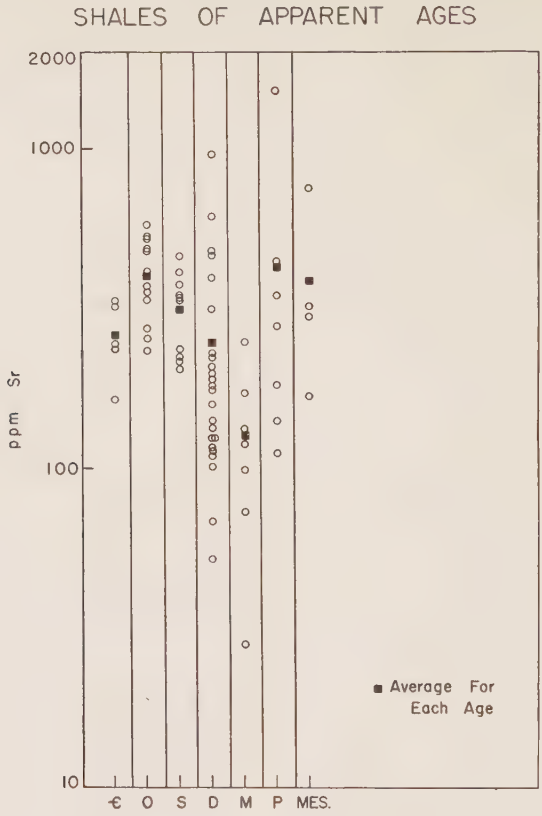

Fig. 21. Comparison of strontium contents of shales of different ages.

Deep-sea Sediments

A reconnaissance study of the distribution and abundance of strontium in deep-sea sediments was made on a single core obtained from the core laboratory at the Lamont Observatory. An Atlantic equatorial core A180–74 was chosen, because it was one of the few available that showed normal pelagic sedimentation without complications by turbidity currents, sifting, etc. Samples were taken periodically down the length of the core. The results appear in Table 13.

It is evident that the main contributor of the strontium is the calcium-carbonate ooze. The core represents only a portion of the Pleistocene. Kulp, Turekian, and Boyd (1952) report much higher values of strontium for pure globigerina ooze of Tertiary age from deep-sea cores.

The average of the ten determinations down the core is 2075 p.p.m. strontium.

This high value could account for the removal of much of the strontium brought to the sea at the present time. However, an additional problem is immediately brought into focus; if the globigerina contribution to pelagic sedimentation has been of importance only since the Mesozoic, then there must have been a different strontium economy in the sedimentation before this time, since no geosynclinal organisms or present-day littoral organisms generally give high values, as observed either in Pleistocene or earlier Tertiary cores. The possible significance of this is discussed later.

Table 13. Strontium content of segments of Atlantic Ocean core A180–74

Depth in core (in cm)	Percentage Ca	p.p.m. strontium
top	39·6	2560
26	28·2	1920
51	35·6	2320
76	32·9	1940
101	34·2	2080
151	37·5	2160
211	35·7	2320
251	31·2	1550
351	38·2	1830
451	36·8	2070

The Abundance of Strontium in the Sedimentary Rocks

Using the data for limestones (Kulp, Turekian, and Boyd, 1952), the average strontium content of "pure $CaCO_3$" limestones is calculated to be 610 p.p.m. Admittedly this is a fictitious rock, but it can be seen that the value for the strontium content of limestone then becomes a maximum value. Since there are many marls and calcareous shales that are difficult to classify, the value for "pure $CaCO_3$" limestones allows the greatest flexibility in geochemical calculation.

The shales present a difficulty of interpretation. Depending on whether a "pure" shale free of calcium carbonate is taken or an "average" shale which includes calcium carbonate, a slightly different average value for strontium will be obtained. These values are not significantly different from each other, but if the ratio of strontium to calcium is compared there is seen to be a difference of a factor of 10.

The method employed in calculating the "pure" shale was derived by considering Wickman's method of correction for "limestone" in shales (1954). He thought the average of CaO/MgO in limestones was around 6. Using this figure and the value of CO_2 for the average shale, he concluded that the average calcium content of carbonate free shale was about 0·52% CaO.

In the present calculation, all shales were averaged for calcium and strontium where the calcium content fell below 1·5% Ca. This gave an average calcium content of 0·4% Ca.

The "average" shale is the simple average of the 69 shales analysed.

Table 14 gives the resulting values for sedimentary rocks.

Table 14. Strontium content of sedimentary rocks

Rock	Avg. %Ca	Avg. p.p.m. Sr	$\frac{\%Sr}{\%Ca} \times 10^3$
"Pure calcium carbonate (155)	40·0	610	1·5
"Pure" shale (35)	0·4	245	61·1
"Average" shale (69)	5·0	300	6·0
Calcareous Pelagic sediments	35·0	2075	5·9

Metamorphic Rocks—Schists

Twenty-five schists were analysed for strontium and calcium. These are all thought to have been sedimentary in origin. It is seen that they generally follow the plot of the shales when log Sr/Ca is plotted against log Ca (Fig. 19). There is no correlation of Sr with Ca, as in the case of the granites; evidently the metasomatism and metamorphism was not adequate to allow mass migrations and the consequent attainment of equilibrium ratios of Sr/Ca.

Since this is the case, it is not probable that ortho-amphibolites and para-amphibolites can be differentiated on the criterion of the strontium-calcium relationship, as was suggested (Turekian, 1955b). At any rate, a careful study must be made to detect any other trends among the trace elements to distinguish between these two types of rock.

Synthesis

Patterns of Distribution and Geochemical Coherence

An empirical relationship has been observed between the dependence of strontium abundance on calcium abundance (geochemical coherence) and the pattern of distribution of strontium in a particular geologic phase. It was seen that, in the case of limestones, pelitic rocks, and basaltic rocks, the strontium content is generally independent of the calcium content.

For these rocks, histograms with the logarithm of the strontium concentration as the variate show symmetric patterns, possibly indicating a lognormal distribution.

In the case of granitic rocks, the strontium content was found to be a function of the calcium content. A histogram with the logarithm of the strontium concentration as the variate showed a skewed pattern. The skewness has been related to the relative choice of high- and low-calcium granitic rock specimens. It is seen then that the distribution pattern for strontium here is either a function of the calcium distribution in the population from which the sample was taken or a function of the bias of such a sampling procedure.

Since it is known that both the strontium and the calcium in deep-sea sediments is found mainly in the calcium carbonate fraction, it is obvious that a distribution pattern for strontium in this geologic phase will be a function of the sampling of high- vs. low-calcium carbonate sediments.

It appears then that for strontium a symmetrical logarithmic distribution pattern is in some way related to the observed lack of geochemical coherence of strontium and calcium, while a skewed logarithmic distribution results from the geochemical coherence of strontium and calcium. (It is obvious that if the calcium were symmetrically distributed, the strontium distribution would also be symmetrical in the geochemically coherent case.) It remains to be seen if this empirical observation can become a generalization when applied to other trace elements.

Estimation of the Crustal Abundance of Strontium

From the above discussion it is evident that the estimation of the crustal abundance of strontium is not a simple task nor one with a singular solution.

Table 21 gives the average Sr and average Ca content for various selections from the data. Because there is no relation between Ca and Sr in basaltic rocks, limestones, and shales, the average value for strontium may be taken as the true abundance of this element in these phases of the lithosphere.

The trouble comes with granitic rocks, where the strontium content is a function of the calcium content. As was stated previously, a simple average of the data for all granitic rocks may only give a reflection of the sampling of the investigator and have no bearing on true crustal abundances. The extent of granitic-rock types and their composition in three dimensions in the continental areas is uncertain.

Proceeding then in an area of some doubt, the premise suggested by several geologists (Worzel and Shurbet, 1955; Poldervaart, 1955) that the continental crust is mainly granodioritic in composition, is adopted. For the sake of calculation, those granitic rocks having between 1% and 5% Ca are averaged for both strontium and calcium.

As the average strontium content for both basaltic rocks and "granodioritic" rocks is about the same, the weighting given these rock types does not affect the calculated strontium abundance of the crust, i.e. 450 p.p.m. This conclusion would not be valid for some other elements, such as rubidium.

With this estimate an accompanying caution must be recorded: the crustal abundance is based on one crustal model, which seems valid to many geologists. If this model should change by "chance or nature's changing course untrimm'd," then so must the abundance estimate.

Additionally this is the estimate of crustal abundance on the basis of a composition possibly peculiar to the present geologic age. It is not easy to ascertain how the crust may have varied in composition with time.

The Cycle of Strontium

Table 15 shows the summary data of the calcium and strontium concentration of various phases of the geologic realm. The ratios of the strontium concentration to the calcium concentration are listed in the last column.

It is evident that strontium is markedly enriched in the crust relative to calcium when compared to the cosmic ratio. The Sr/Ca ratio increases in granitic rocks as a whole relative to basaltic rocks, while pegmatites appear to have a higher ratio than granitic rocks (see analyses CM 1 and NG 11).

"Pure" shales as described in the section on sedimentary rocks have a high

Table 15. Abundance of strontium and calcium in various geologic realms

Rock	Average % calcium	Average p.p.m. strontium	$\frac{\%Sr}{\%Ca} \times 10^3$
Basaltic rocks (245)	7·1	465	6·5
Granitic rocks (175)			
0·1–1·0% Ca	0·6	100	16·7
1·0–5·0% Ca	1·9	440	23·0
Schists	3·1	242	7·9
Sedimentary rocks			
Limestone (150)	40·0	610	1·5
"Average" shale (69)	5·0	300	6·0
"Pure" shale (35)	0·4	245	61·1
Pelagic sediment	35·0	2075	5·9
Sea (Odum)	—	—	20·2
Cosmic (Suess and Urey, 1956)	—	—	0·84

Sr/Ca ratio, indicating that the adsorption sites on clay particles prefer strontium relative to calcium. From this fact it seems possible that strontium is left behind in the weathering products of igneous rocks relative to calcium, since the clay minerals are prominent residues of weathering. Ultimately all the strontium and all the calcium weathered from igneous rocks must be accounted for in the sedimentary realm and the sea. This is the basic premise of geochemical balance calculations.

It is apparent that the geochemical cycle of strontium has been altered during geologic time. It will be useful to discuss the observed changes in the sedimentary realm and the bearing of these changes on the path strontium has taken from igneous rock to sediment at different times during the earth's history.

If, in the pre-Cambrian, shales were considerably more important than calcareous deposits, then a type of secular equilibrium would be set up whence the shales, always able to adsorb more strontium than calcium, would preferentially take up the strontium brought to the sea by weathering. Hence, a low level of strontium would be maintained in the sea relative to calcium during the pre-Cambrian.

At the beginning of the Palaeozoic, or possibly considerably earlier, this pattern was disturbed by the prolific deposition of calcium carbonate by organisms in the sea. Since it has been shown that the strontium admittance is low for this solid phase, the sea might have undergone an enrichment of strontium relative to calcium.

From the Mesozoic forward, if deep-sea sedimentation had become remarkably important and such specimens of pelagic foraminifera as globigerina became prolific, there apparently had been a marked increase in the strontium content

of the sea. This is reflected particularly in the extremely high strontium content of Tertiary globigerina ooze as well as of deep-sea cores generally.

The cause of this increase may be attributed either to an accumulative effect in the sea due to many years of calcite deposition with a low Sr/Ca ratio, or a radical change in source of deposition. It is evident that if basalts were the main source of sedimentation during the Palaeozoic, while granites and granodiorites have been the most important primary sources since the Mesozoic, this would account for the differing amounts of strontium and calcium brought to the sea. This seems to be borne out by recent ideas on the development of continents (Kay, 1951).

It is the tentative conclusion of this section that the Sr/Ca ratio in the sea has been increasing with time, in part due to the appearance of calcium carbonate depositing organisms, but probably mainly due to changes in the kinds of rock exposed to weathering.

The Palaeoecological Significance of Strontium

In the previous section the proposition was made that the Sr/Ca ratio in the sea has been increasing with time. This small change in the composition of the sea may have had considerable import in determining the direction of marine invertebrate evolution. The possible relation between the variations in dominant marine invertebrate faunal types with time and the variations of the Sr/Ca ratio in the oceans is an interesting question.

Most marine invertebrates that have left any record in the geologic column have been those depositing calcium carbonate tests. It is generally known that there are two polymorphs of calcium carbonate, viz. calcite and aragonite, which are prominent in the tests of organisms. Some organisms deposit only calcite, others deposit only aragonite, while others deposit a complex mixture of the two types.

From an overall view it seems that aragonite deposition by organisms is more prominent today than during the Palaeozoic. Lowenstam (1954) has recently called attention to this fact, documented in part by Bøggild's observations (1930).

In the case of coelenterates, the calcitic tabulates and the rugose corals were the main forms during the Palaeozoic. These two groups became extinct by the Mesozoic. In their place the abundant calcium-carbonate depositers became the scleractinian corals, which produce aragonitic tests, and alcyonarian corals, some of which also deposit aragonite.

It also appears that though mollusks were present during the Palaeozoic, the brachiopods were more abundant. Many mollusks have aragonitic tests, whereas brachiopods are exclusively calcitic.

The modern foraminifera such as the globigerinids, though depositing calcitic tests, are higher in strontium content by far than the Palaeozoic fusulinids.

Trueman (1942) has suggested that the absence or presence of strontium in an environment from which calcium carbonate is depositing will determine whether calcite or aragonite will be the preferred crystal form. Odum (1950) has done experiments to show that a limited solid-solution series exists between strontianite and aragonite. These two minerals crystallize in the same system, viz. orthorhombic, whereas calcite is hexagonal.

Recently, Murray (1954) has documented the effect of Sr, Pb, and Mg in determining the particular polymorph of calcium carbonate that will be deposited from solution. The presence of any of these three elements greatly enhances the formation of aragonite in preference to calcite.

Using this information, we can speculate on its significance. During the Palaeozoic the low Sr/Ca ratio of the sea encouraged the precipitation of calcite relative to aragonite. The most prolific organisms of that time were those depositing this polymorph of calcium carbonate.

Eventually, probably by the end of the Palaeozoic, from palaeontological evidence, the Sr/Ca ratio had become high enough to encourage those fauna depositing aragonitic tests. Subsequently these types have remained dominant, together with calcitic forms (such as globigerina), which are able to tolerate high strontium.

Hence the behaviour of strontium may have directed in part the direction of evolution of marine invertebrates by providing an environment in which aragonite-depositing or strontium-tolerating tests were built with greater success than the previous forms.

Summary and Conclusions

A study of the abundance and pattern of distribution of strontium in the earth's crust has revealed the following relationships:

1. In basaltic rocks the strontium content is essentially independent of the calcium content, whereas in granitic rocks a definite relation exists between strontium content and calcium content.

2. Basaltic rocks of a particular geologic province have the same strontium concentration within narrow limits. There are definite differences between the means of various areas.

3. Basaltic rocks, shales, and limestones all show a noncoherence of strontium with calcium for universal sampling, and all three give evidence of nonskewed lognormal distributions. The abundance of strontium in these three phases is: basaltic rocks, 465 p.p.m.; shales, 300 p.p.m.; and limestones, 610 p.p.m.

4. Strontium follows calcium in both granitic rocks and deep-sea sediments. Distribution curves obtained for strontium in either of these materials is a function of sampling bias or calcium distribution. If low-calcium granites are considered as the major contributors of continental rock, the abundance of strontium is 100 p.p.m. But if the more plausible alternative of a mainly granodioritic continental crust is chosen, the strontium abundance is 440 p.p.m.

5. The crustal abundance of strontium on the assumption of a basaltic and granodioritic crustal composition is 450 p.p.m.

6. It is proposed that the source of sedimentation during the Palaeozoic had a lower Sr/Ca ratio than the post-Palaeozoic source. The former may have been dominantly basaltic, while the latter has a larger granite or granodioritic component.

7. The increase in the Sr/Ca ratio in the sea at the end of the Palaeozoic is proposed as being a possible cause for the change from the dominance of calcite-depositing marine invertebrates to the modern condition of dominance by aragonite depositing organisms and organisms with calcitic tests with a high strontium tolerance.

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Melting relationships of Ni-Mg olivines and some geochemical implications

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Abstract—A complete series of solid solutions exists in the range Ni_2SiO_4–Mg_2SiO_4. Temperatures of beginning of melting increase with increasing content of Mg_2SiO_4. Solid solutions in the range N_{100}–$N_{50}M_{50}$ melt incongruently with the separation of NiO. In this range, ternary relations obtain. In the range $N_{50}M_{50}$—M_{100} the system is binary. The behaviour of nickel in magmas is discussed in terms of the experimental data obtained, and it is concluded that nickel enters common olivine at the expense of iron rather than magnesium.

Introduction

Since the pioneer study of Vogt (1923) a considerable amount of data relating to the behaviour of nickel in magmas has been published. It is known that nickel becomes highly concentrated in the earliest ferromagnesians to crystallize, particularly in olivine. The nickel occupies Mg-Fe positions in the lattice and displays a much higher tendency to enter crystals than either of its two host elements (Wager and Mitchell, 1951). It is generally considered that camouflage of Ni by Mg in ferromagnesian minerals explains this behaviour. Recently, however Ringwood (1955) has pointed out some difficulties in this interpretation on the basis of crystal chemical and melting relationships of Ni and Mg compounds. Consequently, an experimental investigation of melting relationships of Ni-Mg olivines seemed desirable in order to clarify the situation. The results obtained verify the previously stated views of the author. In addition, they have some bearing on the "camouflage" concept applied to solid-solution series.

Experimental

(a) *Methods*

The pure components MgO, NiO, and SiO_2 were thoroughly ground together under benzene in the desired proportions and formed into tablets in a small press. Tablets of the composition M_{100}, $M_{80}N_{20}$, $M_{60}N_{40}$, $M_{40}N_{60}$, and $M_{20}N_{80}$, were prepared ($M = Mg_2SiO_4$, $N = Ni_2SiO_4$). The figures given correspond to weight per cent. The tablets were sintered for one hour at 1600°C in a graphite resistance furnace, then recrushed, and the process repeated three times. Microscopic examination of the products indicated uniform phase distribution, although complete conversion to olivine was not obtained. X-ray powder patterns, however, revealed a high degree of conversion. In view of the accuracy of the temperature measurements in the furnace (±20°C), further heat treatment aimed at complete conversion was deemed unnecessary.

It was found impossible to prepare pure Ni_2SiO_4 by this method. Fusing the components together in an oxyacetylene flame was also not successful. Ni_2SiO_4 was finally made, using Grigoriev's (1937) method—the oxides were mixed with 2% CaF_2 and sintered for several hours at 1400°C.

Runs were carried in a platinum-60% rhodium-40% strip furnace (Roberts and Morey, 1930) and temperature was measured using a Leeds and Northrup optical pyrometer. Calibration of the pyrometer was against a mixture of MgO 15% and SiO_2-85% which melts at 1698 ± 5°C. Results indicated a fairly close approximation to black-body conditions within

the strip. The precision of the temperature measurement by this method is not high—about $\pm 20°C$. This was sufficient, however, for the purposes of the experiment.

The temperatures of beginning of melting are rather easily obtained, but those corresponding to the completion of melting are more uncertain. Quenching was carried out by cutting off the current and simultaneously immersing the resistor strip in water when required. It was not always successful with the compositions high in Mg_2SiO_4, but usually it was possible to distinguish between primary crystals and devitrified liquid.

The runs were made in the shortest time necessary to achieve equilibrium, in order to minimize absorption of nickel from the charge by the strip. The average size of the charges was about 1 mg. It was found that the addition of 2% CaF_2 to the mixtures lowered the temperature of beginning of melting less than 20°C on the average—i.e. within the limits of error of temperature measurement. The runs with pure Ni_2SiO_4 were made with material prepared as previously mentioned—by sintering the oxides with 2% CaF_2.

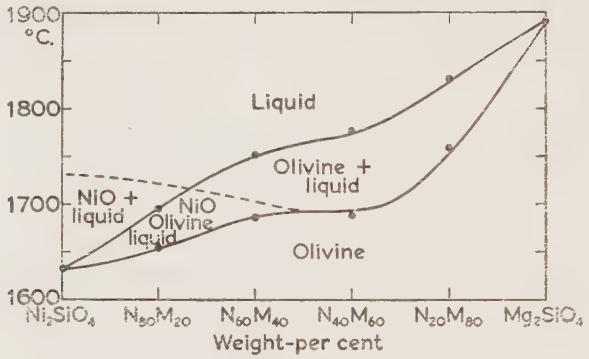

Fig. 1. Approximate pseudobinary diagram depicting phase equilibria along Ni_2SiO_4—Mg_2SiO_4 join in system NiO—MgO—SiO_2.

(b) *Results*

Results of the experiments are set out in Table 1. The equilibrium diagram based upon the results is depicted in Fig. 1.

The principal conclusions are as follows:—

1. Ni_2SiO_4 and Mg_2SiO_4 form a complete series of solid solutions.

2. In the composition range $N_{50}M_{50}$ to M_{100} the system is binary. Melting behaviour is of the Roozeboom type 1. The temperatures of beginning of melting and completion of melting decrease with increasing content of Ni_2SiO_4.

3. In the range $N_{50}M_{50}$ to N_{100}, the olivine solid solutions melt incongruently with precipitation of NiO. Above the solidus within this range is a ternary field in which NiO, Ni_2SiO_4—Mg_2SiO_4 solid solutions, and liquid coexist.

It should be emphasized that the courses of crystallization can only be followed on the ternary diagram MgO—NiO—SiO_2 for compositions between N_{100} and $N_{50}M_{50}$. Fig. 1 depicts the phases present in this ternary region, but does not give the composition of the liquid. In the binary part of the field, however, composition of coexisting solids and liquids can be read off the diagram.

The inflexion between $N_{60}M_{40}$ and $N_{40}M_{60}$ in the liquidus and solidus of Fig. 1 is smaller than the possible margin of error in temperature determination. However, this inflexion appears to be a real feature. Several runs indicated that the temperatures of beginning of melting for both these compositions were approximately similar.

Table 1. Results of experiments on mixtures having compositions between Ni_2SiO_4 and Mg_2SiO_4
(The term "olivine" refers to Mg_2SiO_4-Ni_2SiO_4 solid solutions)

Composition (wt. %)	Temp. (°C)	Phases present
Ni_2SiO_4 (N) + 2% CaF_2	1700	Brown glass, a little NiO (reaction with strip)
	1700	Liquid, NiO
	1630	Liquid, NiO
	1620	Olivine
	1590	Olivine
N_4M_1	1720	Liquid, small amount of NiO
	1710	Liquid, NiO
	1700	Liquid, NiO
	1690	Olivine, NiO, liquid
	1670	Olivine, NiO, liquid
	1660	Olivine, NiO, liquid
	1650	Olivine + small amt. liquid + NiO
	1640	Olivine
N_3M_2	1760	Liquid
	1750	Olivine, NiO, liquid
	1730	Olivine, NiO, liquid
	1710	Olivine, NiO, liquid
	1700	Olivine, NiO, liquid
	1690	Olivine, NiO, liquid
	1680	Olivine
N_2M_3	1790	Liquid
	1770	Olivine, liquid
	1750	Olivine, liquid
	1730	Olivine, liquid
	1710	Olivine, liquid
	1690	Olivine, liquid
	1680	Olivine
N_1M_4	1830	Liquid
	1810	Olivine, liquid
	1790	Olivine, liquid
	1770	Olivine, liquid
	1760	Olivine, liquid
	1750	Olivine
M_5	1890	m. p. determined by Bowen and Schairer (1935)

The upper extent of the NiO field is only tentatively indicated (dotted line). This portion of the system requires more detailed study. Difficulty was experienced with the Ni-rich compositions at high temperatures due to absorption of Ni by the strip. For the purposes of this study, however, the other half of the system is of greater significance.

In the case of composition N_3M_2 (Table 1) it will be noticed that crystals of NiO are present at temperatures above the stability field of NiO on Fig. 1. It is believed that equilibrium was not always attained with this composition. Invariably at the higher temperatures, the NiO crystals are included in residual

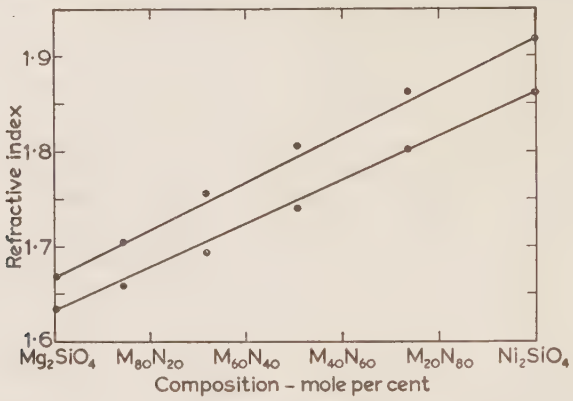

Fig. 2. Alpha and gamma refractive indices of Mg_2SiO_4—Ni_2SiO_4 solid solutions.

olivine crystals; they are never found in contact with the liquid. Apparently the olivine is protecting the NiO from solution. There is only a small range for this composition where the olivine melts to form NiO + liquid. Probably, if substantially greater time were allowed for the runs, equilibrium would be reached. However, this was impracticable because of reaction of charge with strip and difficulty of keeping the furnace temperature constant for long periods.

The α and γ refractive indices of the olivine solid solutions have been plotted in Fig. 2 on a mole percentage basis. There is a linear relationship indicative of complete solid solution. The slight deviation from linearity of some of the points is probably due to inhomogeneity in the sample. The Ni_2SiO_4-rich samples were unsuitable for accurate measurement of refractive indices, and results can be considered accurate to $\pm 0{\cdot}01$. The Ni_2SiO_4 was formed by sintering the components in their correct proportions with 20% of boric oxide for several hours at 1400°C, followed by leaching with hydrochloric acid.

Discussion

(a) *The Behaviour of Nickel in Magmas.*

Discussion will be restricted to olivines, but similar reasoning probably applies to pyroxenes.

Basic magmas commonly contain 0·005–0·05% Ni. Most of the nickel becomes incorporated in the highly-magnesian olivines which crystallize at an early stage. The nickel may be regarded as occurring in the form of Ni_2SiO_4 in solid solution.

In 1923, Vogt demonstrated that a close relationship existed between Ni and Mg and that the Ni concentration in the olivines decreased as the Mg decreased and Fe increased.

During recent years detailed studies of trace-element distribution during magmatic crystallization have demonstrated that nickel possesses a much greater tendency to enter early olivines (also pyroxenes) than magnesium. In igneous-rock series formed by fractional crystallization of basic magma, it is found that the Ni/Mg ratio decreases rapidly as fractionation proceeds (e.g. Nockolds and Allen, 1953, 1954). The comprehensive study by Wager and Mitchell (1951) demonstrated that the tendency of nickel to enter both olivine and pyroxene was double that of magnesium. On the basis of this data, it might be concluded that Ni behaves in magmas as though its compounds had higher melting-points than the corresponding magnesium compounds into which it enters in solid solutions. The relationships described above have been widely interpreted in terms of "camouflage" of Ni by Mg in olivine. Goldschmidt (1944) suggested that the relative enrichment of Ni was due to the Ni-O bond being stronger than the Mg-O bond because of its more covalent nature.

Ringwood (1955) has pointed out that the relative enrichment of nickel in early ferromagnesians is not consistent with the melting relationships of Mg and Ni compounds which would be expected from crystal chemical data. Because of the lower electronegativity of magnesium, the Mg-O bond in crystals should be stronger than the Ni-O bond, and therefore magnesium compounds should possess greater thermal stability (and therefore higher melting-point) than corresponding compounds of nickel. Consequently, it would be expected that in the solid-solution series Mg_2SiO_4—Ni_2SiO_4 the earliest crystals to separate would be richest in Mg_2SiO_4. This prediction has been completely verified by the experimental work described earlier.

Therefore, it is apparent that the experimentally determined phase relationships are contrary to the known behaviour of nickel in magmas.

(b) *Cause of Disagreement*

This disagreement between magmatic and experimental behaviour of nickel is almost certainly due to the fact that experimental-phase relationships obtained in the simple system are not necessarily valid when applied to a highly complex magmatic system which is crystallizing at temperatures lower than those employed in the experimental work.

There are two aspects of this statement to discuss. The presence of other components lowers the temperatures of crystallization. It is possible that the phase relationships might be different at lower temperatures—a field of solid immiscibility might be developed with two series of solid solutions on either side in eutectic relationship. In this case, however, the direction of the curves near the Mg-rich end remains essentially unaltered. Consequently, the difference in crystallization temperature between the magmatic and experimental systems cannot be responsible.

The presence of extra components may affect the phase relationships for reasons other than temperature, however. This applies particularly to iron.

The average olivine crystallizing from basic magmas contains about 10–20% of Fe_2SiO_4 in solid solution. It seems likely that the anomalous behaviour of nickel in magmas is somehow connected with the presence of this Fe_2SiO_4.

Although the effect of other components of the magma cannot be entirely disregarded, it seems unlikely that they could profoundly alter the relationships in the simple system, since they are unable to enter the olivine structure. The rôle of Fe_2SiO_4 may now be discussed.

The system Mg_2SiO_4—Fe_2SiO_4 was demonstrated by Bowen and Schairer (1935) to be of the Roozeboom Type 1. They demonstrated that small amounts of Fe_2SiO_4 in solid solution in Mg_2SiO_4 are capable of causing marked reductions in the temperatures of beginning of melting. Thus, an olivine containing 20 mole per cent of Fe_2SiO_4 begins to melt at 1600°C, a lowering of about 300°C. Most olivines crystallizing from basic magmas possess fayalite contents of the order of 20 mole per cent, and it is clear that the temperature of beginning of melting of these olivines is below that of Ni_2SiO_4 (1640°C).

It therefore seems that the presence of iron in olivine lowers its overall thermal stability to such an extent that nickel is able to enter in excess. Thus, the presence of a relatively small amount of iron is sufficient to reverse the relationship between Mg_2SiO_4 and Ni_2SiO_4 found in the simple system.

A complete understanding of this behaviour could only be obtained by study of the ternary system Mg_2SiO_4—Ni_2SiO_4—Fe_2SiO_4, but the previous discussion will serve as an approximation.

The situation may be considered on an atomistic basis. In ordinary olivine, the Mg and Fe ions are distributed randomly among the appropriate lattice positions. However, there is a big difference in the tenacity with which they hold these positions. The Mg ions are strongly bonded and relatively immobile, whereas the Fe ions are more weakly bonded (Ringwood, 1955) and possess greater mobility. The melting behaviour is a consequence of these relationships.

Consider the case where a small amount of nickel is added to a melt which is in equilibrium with an Mg-Fe olivine. The nickel will enter the olivine, occupying Mg-Fe positions. However, it will not replace Mg and Fe on an equivalent basis. The Fe ions, being weakly bonded and mobile, will be readily replaced by Ni, whereas only a relatively small amount of Mg ions will leave the structure. According to this interpretation of the experimental evidence, nickel enters the olivine lattice at the expense of iron rather than magnesium. In this sense, therefore, it may be claimed that nickel is camouflaged principally by iron in olivine rather than by magnesium.

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Pre-Cambrian atmosphere: evidence from the Pre-Cambrian of Sweden

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Abstract—Sedimentary haematite ores of central Sweden give evidence of the existence of an oxidizing atmosphere about 2000×10^6 years ago. This is not consistent with Rankama's conclusions from the unoxidized condition of a diorite conglomerate in Finland. Therefore a (later) Pre-Cambrian conglomerate in northern Sweden has been examined for comparison. Where it is made up of dioritic material no proofs of oxidation can be found, but where the material is mainly iron-ore pebbles, magnetite ore is found to have been completely oxidized to haematite (martite) before being embedded as pebbles in the conglomerate.

The evolution of the earth's atmosphere in Pre-Cambrian times is one of the most interesting objects for geochemical study. It is now generally regarded as an established fact that this atmosphere at first was devoid of oxygen. Also it is clear that already before the beginning of the Cambrian, atmospheric conditions were essentially as they are today. The problem, then, is this: when, within the time of about 4×10^9 years that preceded the Cambrian, did the amount of oxygen in the atmosphere reach such height that its effects could be registered in the rocks, and that animal life was possible?

The question has been variously answered. Thode *et al.* (1953) place the change from a reducing to an oxidizing atmosphere very late in the Pre-Cambrian, only 700 or 800×10^6 years ago, basing this conclusion on their study of the isotopes of sulphur. Rankama (1955) regards the high proportion of ferrous to ferric iron in a diorite conglomerate of Suodenniemi in Finland as proof that weathering in Bothnian time, that is, about 1900 or 2000×10^6 years ago, took place in the absence of atmospheric oxygen. A. M. MacGregor (1927) at a time when reliable age determinations in the Pre-Cambrian were still lacking, discusses the Pre-Cambrian atmosphere in the light of the quartz-banded ironstones: "The stumbling-block, upon which most of the theories put forward [on the origin of these ironstones] come to grief, appears to the writer to be the tacit assumption that the rocks were necessarily formed beneath an oxygenated atmosphere. If, on the other hand, it is assumed that the atmosphere was devoid or nearly devoid of oxygen and was rich in carbon dioxide, the difficulties of the problem become almost insignificant." MacGregor also refers to the fact that "iron-depositing bacteria are capable of precipitating iron in the ferric state in the absence of free oxygen."

Several writers have commented upon the short time available for the evolution leading up to the highly diversified Lower Cambrian fauna, if atmospheric oxygen had not been available until 700 or 800×10^6 years ago.

Serious objections have also been raised on purely geological grounds. Among other arguments, the development of oxidic iron sediments at an early stage has been referred to. Urey (1952a) maintains that the "precipitation of limestone

in great quantities presents the greatest difficulty to the hypothesis of a long period during which a reducing atmosphere was present." The same author (1952b) also states that "the presence of highly oxidized iron in red beds and haematite (Fe_2O_3) iron ores is justly regarded as evidence of atmospheric oxygen. . . . Most of the great bodies of iron ore were laid down in the late Pre Cambrian (Huronian) or were extensively eroded during this time. The iron ore of the Vermilion range of Minnesota is much earlier (Keewatin), and thus oxidation of ferrous iron to ferric oxide took place early in the earth's history." R. T. CHAMBERLIN (1952) also points out that evidence of this nature is not restricted to the later Pre-Cambrian: "Extensive Archean iron ores in the ferric state (hematite, for Fe_2O_3) testify, however to an abundance of atmospheric oxygen in these early times." Oxidic iron sediments are also among the phenomena referred to by RUBEY (1955): "Just how soon thereafter [after the forming of the first atmosphere] oxygen began to accumulate is a problem about which it seems advisable to withhold judgment until the evidence from the earliest rocks has been appraised more extensively. The presence . . . of sedimentary iron oxides in the Pre Cambrian iron formations . . . suggests that at least some oxygen must have been available fairly early in geologic time."

As seen from the above, discussion on the subject, apart from such an early contribution as MACGREGOR'S paper, has arisen only recently. Previously, those engaged in the study of the Pre-Cambrian have tacitly assumed that for the nature of the atmosphere, as for conditions in general except those dependent upon the existence of various forms of life, the uniformitarian principle of HUTTON could be applied. One fact that has greatly contributed to this attitude has been the essentially normal character of the Pre-Cambrian sediments (for these, see ESKOLA, 1932). It is therefore to be expected that there are scattered, all over the extensive literature on the Pre-Cambrian, records of observations that have a bearing on the nature of the atmosphere but which were not originally presented as such because this nature was taken for granted. It is the purpose of this paper to present some examples from the Pre-Cambrian of Sweden.

The quartz-banded haematite ores of Central Sweden are in all respects, except their generally higher percentage of iron, similar to the well-known haematitic "banded jaspers" of the Lake Superior region. They are interstratified in the leptite formation, which is mainly built up of siliceous volcanics and forms the oldest unit of the Svionian cycle. Complicated geological events, and therefore also a considerable length of time, separate them from the end-stage of this cycle, the Late Svionian phase of migmatitization and intrusion, which has been dated to around 1700 or 1800×10^6 years ago (PARWEL and WICKMAN, 1954). The age of the ores, therefore, can be estimated to be around 2000×10^6 years.

The ores in question contain their iron generally in the form of specular haematite, but also magnetite is mostly present, and in some deposits is the only ore mineral.

The haematite of the ore layers is always recrystallized, but such forms as the clouds of red haematite dust that determine the colour of red jasper layers appear to be still in their original development. The magnetite, again, generally is formed as a result of metamorphism of haematite ore. In most deposits it develops preferably along the margins of the ore body and along intersecting granite and

pegmatite dikes. In strongly deformed deposits the ore often forms lenses built up of a core of haematitic ore and a mantle of magnetite. It is thus clear that the magnetite, at least as a rule, is a product of metamorphism of an originally oxidic deposit.*

Valuable information on the actual subject can be obtained from a study of the Stripa deposit, which also has been examined in more detail than any other representative of this ore-type in Sweden (Geijer, 1938). As to the original form in which the iron was deposited, Stripa supplies very strong arguments for the view that it has been as haematite or possibly ferric hydroxide.† An origin from a silicate is ruled out by the purity of the regular haematite layers. The possibility that the original form was siderite appears to be excluded by the common occurrence of extremely thin and regular layers of haematite in the quartz bands of one of the main ore types of the deposit. For it seems inconceivable that oxidation of siderite could have taken place without any spreading of the oxidized compound outside these thin layers (Geijer, 1938). In all probability these views may be applied also to the other haematite ores of the region, although the case is not always equally clear.

While previous investigators of the banded jaspers of the Lake Superior region generally have regarded most of the haematite in them as a product of oxidizing weathering, James (1954) has recently, in a detailed study of the iron formations, found that haematitic jasper in considerable quantities also occurs as a primary phase of these sediments. Like the present writer, James calls attention to cases of very fine alternation of haematite and quartz layers as proofs of an original ferric state.

The question may perhaps be asked whether sedimentary deposition of primary haematite (or ferric hydroxide) necessarily involves an atmosphere containing free oxygen. As already quoted, MacGregor means that this is not the case, and refers to the oxidizing activity of certain bacteria. This was written at a time when primary ferric iron was believed to be rather rare in the banded jaspers. And while the reality of such reactions is proved, the quantitative importance of biological processes in the building up of sedimentary iron formations is unknown. Also, there is ample evidence that iron is being precipitated through inorganic factors normally active in surface waters. For the quartz-banded ores in particular, the process indicated by MacGregor seems most unlikely. To judge both from the character of such deposits and from experimental work by Moore and Maynard (1929), there is a common, or at least a comparable, cause for the precipitation of iron and silica. Also there are indications, such as the regularity of the alternating deposition of these two constituents, and the striking scarcity of mechanically deposited material, that sedimentation proceeded rapidly for such a chemical process.

Yet, however convincing the proofs of primary ferric iron in this ore-type

* The most complete survey of this ore type in Sweden has been given (in Swedish) by Geijer and Magnusson (1944); a short summary in English has also been published by the same authors (1952).

† Since the haematite of the ore layers is recrystallized, one cannot exclude the possibility that the original iron mineral was hydroxide. The occurrence of fine haematite dust makes this improbable, however. Attention may also be called to similarities to the haematite ores of the Lahn-Dill region in Germany, the haematite of which is certainly primary (compare Schneiderhöhn, 1941, and literature quoted by him).

may appear to those familiar with all its properties, others may perhaps not accept the geochemical conclusions as definite. Let us therefore suppose that all the iron at Stripa was originally deposited at siderite, and trace the further geological history of the deposit from this starting-point.

At Stripa, folding has been much less intense than in most Swedish deposits of this type. This probably explains why there is very little development of a marginal magnetitic phase. On the other hand, a change to magnetite, accompanied by a removal of quartz and a consequent raising of the iron percentage even up to top grade, has taken place in certain restricted portions of the ore body, generally in a close connection with strike faults related to the folding. This development was completed, and the ore body was practically as it appears today, before the intrusion of Late Svionian aplite dikes. Deformation and metamorphism therefore took place in an ore body, the iron of which must have been in the state of haematite. If, as here assumed for the sake of argument, it was originally sideritic, it must have passed through a surface oxidation before being brought down to greater depths.

In any case, therefore, Stripa presents evidence of an oxidizing atmosphere around 2000×10^6 years ago.

The iron formations of the North American Keewatin, approximately contemporaneous with the leptite formation of the Svionian, appear to give the same kind of evidence. To quote James (1954): "It seems reasonable to conclude that at the time of accumulation of the Pre Cambrian iron formations, the atmosphere was not greatly different from that prevailing today. . . . The atmosphere may well have been of quite different composition at some early stage of the earth's history, but that stage, if it existed, appears to predate the later Pre Cambrian." Truly, James speaks only of the "later Pre Cambrian," which, as generally understood, does not include the Keewatin, but it seems apparent that his conclusions must be valid also for the haematitic jaspers of this earlier stage. Reference may also be made to Urey's express mentioning of the Keewatin iron formation of the Vermilion Range in Minnesota, quoted above.

The conclusions here arrived at from the haematite ores evidently are at variance with those drawn by Rankama from his study of the Suodenniemi conglomerate, which also belongs to the Svionian cycle and probably to a somewhat later stage than the haematite ores of central Sweden. Observations of great interest in this connection have been made on the basal conglomerate of the Vakko sedimentary series in the Kiruna region of northernmost Sweden. This series belongs to the Karelian cycle, the rocks of which occupy large areas in the eastern and northern parts of the Fennoscandian Shield. It is later than the Svionian, probably in these parts following next to this cycle. What can be learned about conditions of weathering in Karelian times therefore has no direct bearing on the Svionian, but indirectly it throws light on the contrasting evidence just referred to.

The basal conglomerate has been examined at four localities. On the lower slopes of Luossavaara iron-ore mountain at Kiruna, where its basement is formed by the volcanics associated with the iron ores of the district, the conglomerate is mainly built up of pebbles of haematite ore (Lundbohm, 1910; for more detailed map, in this part by Zenzén, compare Geijer, 1910). In the Vakkojärvi and

Kovo sedimentary zones, about 20 km north-north-east of Kiruna, the basement is granite and the sediments start with arkose, sometimes highly calcareous, and with conglomerates almost exclusively made up of granite pebbles (Geijer, 1927). Finally, at Maattavaara, 40 km east of Kiruna, the basal conglomerate rests on a diorite and is made up of material derived from this rock (Ödman,1953).

In the Vakkojärvi zone, the best exposure of the contact between the granite basement and the overlying sediments shows the following. The granite is strongly weathered. Microcline and quartz only are often broken up and not chemically altered, but the plagioclase is replaced by a fine sericitic felt. In the interstices between the microcline and quartz grains, and filling fissures in them, there is much calcite, and associated with it are rhombohedra of a ferriferous carbonate. It is not possible to decide if the carbonate also is a product of weathering. More likely it represents an infiltration from the covering sediments which start with a bed about one metre thick, of sandy limestone, followed by coarse arkose and granite conglomerate in alternation, both with a calcareous cement.

Samples of pebbles from the Maattavaara conglomerate have kindly been put at the writer's disposal by O. Ödman. The rock is made up of plagioclase in thick-set tabular grains, biotite in small plates—apparently derived from the alteration of primary pyroxene or hornblende—magnetite, and quartz. The primary magnetite grains do not show any martitization, nor are there any signs of chemical weathering.

This conglomerate then, in the absence of any traces of oxidizing weathering, gives the same kind of evidence as the Suodenniemi conglomerate according to Rankama's interpretation, and the weathered granite described above shows no features that indicate oxidizing conditions.

But the conglomerate of Luossavaara tells a different tale. Earlier investigators had taken for granted that the haematite pebbles of this conglomerate were derived entirely from the small but numerous haematite deposits (Hauki haematite ores) in the immediately underlying volcanics. It was found by Zenzén, however, that also a considerable portion must have come from the huge magnetite ore bodies lower down in the volcanic basement. The present writer, in a general survey of the geology of the region (Geijer, 1931), quoted this observation, and concluded that the magnetite ore bodies, exposed by erosion, must have been superficially changed to martite before the deposition of the first Vakko sediments. For primary haematite, in the ore bodies in question, occurs only as small veins and never in the massive ore. On the other hand, a certain part of the Kiirunavaara ore body is now incompletely martitized from the surface down to considerable depth (Geijer, 1924, 1931). No special study to verify this conclusion about pre-Vakko oxidation was undertaken, as, once there was proof that the ore bodies had been exposed at that time, martitization was deemed a natural consequence. With the question now facing us, however, it became necessary to see whether direct proofs exist or not.

Accordingly, some polished sections were prepared from the conglomerate on Luossavaara. Examination shows that many pebbles must be derived from the primary "Hauki" haematite ores, as they are made up of haematite with obviously primary grain shapes. But it is equally clear that many other pebbles are martitic.

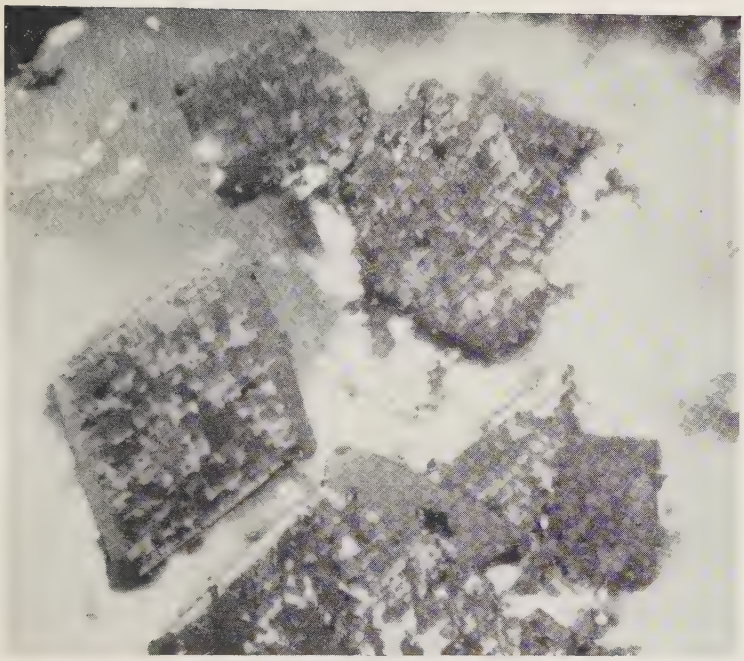

Fig. 1. Martite grains, pebble in conglomerate, Luossavaara at Kiruna. Polished section, nicols crossed, × 185. The sets of secondary haematite lamellae show up in shades from white to black.

facing page 308

Sometimes such a pebble may exhibit throughout an octahedral grain shape, and these octahedra are found to consist of interlocking sets of thin haematite lamellae, the whole giving a characteristic striped mottling when the section is examined with crossed nicols (Fig. 1). This is the pattern arising when alteration to haematite has proceeded along the four plane directions of octahedral magnetite until replacement is complete, and is a sure proof of martitization (compare also Schneiderhöhn and Ramdohr, 1931). The conglomerate thus contains pebbles of originally magnetite ore, now completely oxidized to haematite. This oxidation cannot be referred to conditions nearing the present relief of the country, as is shown by a comparison with present local martitization in the Kiirunavaara ore body, where oxidation has been accompanied by a leaching of apatite and thus led to a characteristic porosity. It must therefore have taken place before the pebbles were incorporated into the conglomerate.

In the opinion of the writer, such positive evidence of an oxidizing atmosphere as has here been reported from the sedimentary haematite ores of Svionian age and from weathering preceding the deposition of Karelian sediments must be considered more decisive than the negative proofs that may, in both cases, be adduced from the diorite conglomerates of the same cycles. It falls outside the scope of this paper to enter upon a discussion of the possible explanation of the conflicting evidence. A clue is perhaps indicated by Rankama's statement that, in the case of the Suodenniemi conglomerate material, weathering may have been more mechanical than chemical. Various possible climatic factors may also have to be considered, perhaps also the influence of even a very primitive plant life. As to the presence of a ferruginous carbonate in the weathered granite below the Vakko sediments at one locality, it must be remembered that it may represent a later infiltration.

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Fugacities and free energies of CO_2 at high pressures and temperatures

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Abstract—Fugacity and free-energy values have been calculated from *p-v-t* data for CO_2 in the temperature range from 50 to 1000°C, at pressures from 25 to 1400 bars.

Introduction

With the increase in experimentation at relatively high pressures (up to 3000 atm) it is to be expected that new data will become available on various reactions in this region. One of the important types of reactions being studied is that involving "decarbonization" of important mineral phases, for example:

$$CaMg(CO_3)_2 \lessgtr CaCO_3 + MgO + CO_2$$

$$3CaCO_3 + 2CaSiO_3 \lessgtr 2Ca_2SiO_4 \cdot CaCO_3 + 2CO_2.$$

Kennedy (1954) has recently determined experimentally the *p-v-t* relations of CO_2 up to 1000°C and 1400 bars. Other functions may be calculated in order to be able to utilize the data for the volatile involved, in more convenient form than that presented by Kennedy. For many calculations of the thermodynamic parameters of the reacting phases or extrapolation of the experimental results, it is desirable to express these data as fugacities and free energies of CO_2 as a function of pressure and temperature.

Procedure

Several methods are available for obtaining these functions from the *p-v-t* data of Kennedy (*loc. cit.*), which are presented as specific volumes at a series of temperatures and pressures. Holser (1954) has recently calculated the fugacities of water from similar data. He used the relationship

$$RT \ln \frac{f_{T,P}}{f_{T,P_0}} = \int_0^P v \, dp$$

integrating the vdp term graphically beyond a certain minimum pressure (100 bars). Due to the fact that the curves cannot easily be extrapolated to zero, he chose to use an equation of state which fitted the volume data for the low-pressure region. MacDonald (1955) has determined the free energies of water directly from the *p-v-t* data from the relationship:

$$F = F^0 + \int_0^P v \, dp$$

where F^0 is the known standard free energy at pressure P_0.

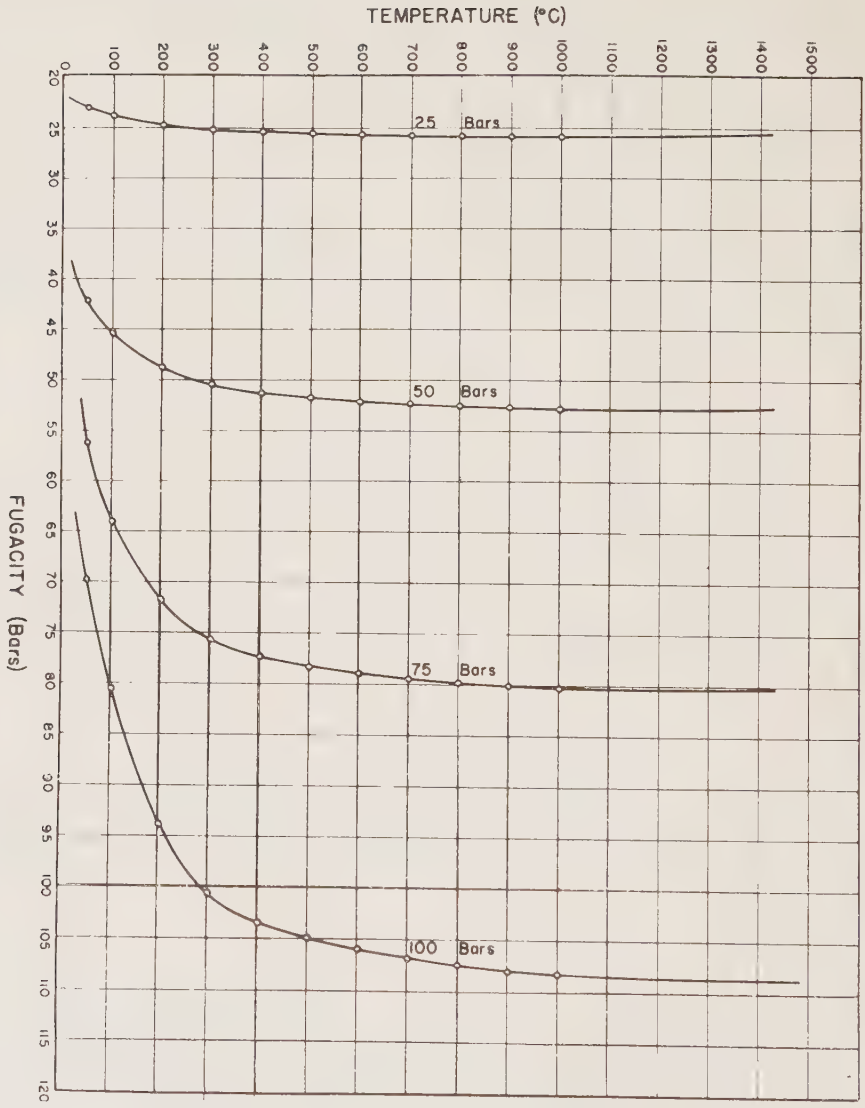
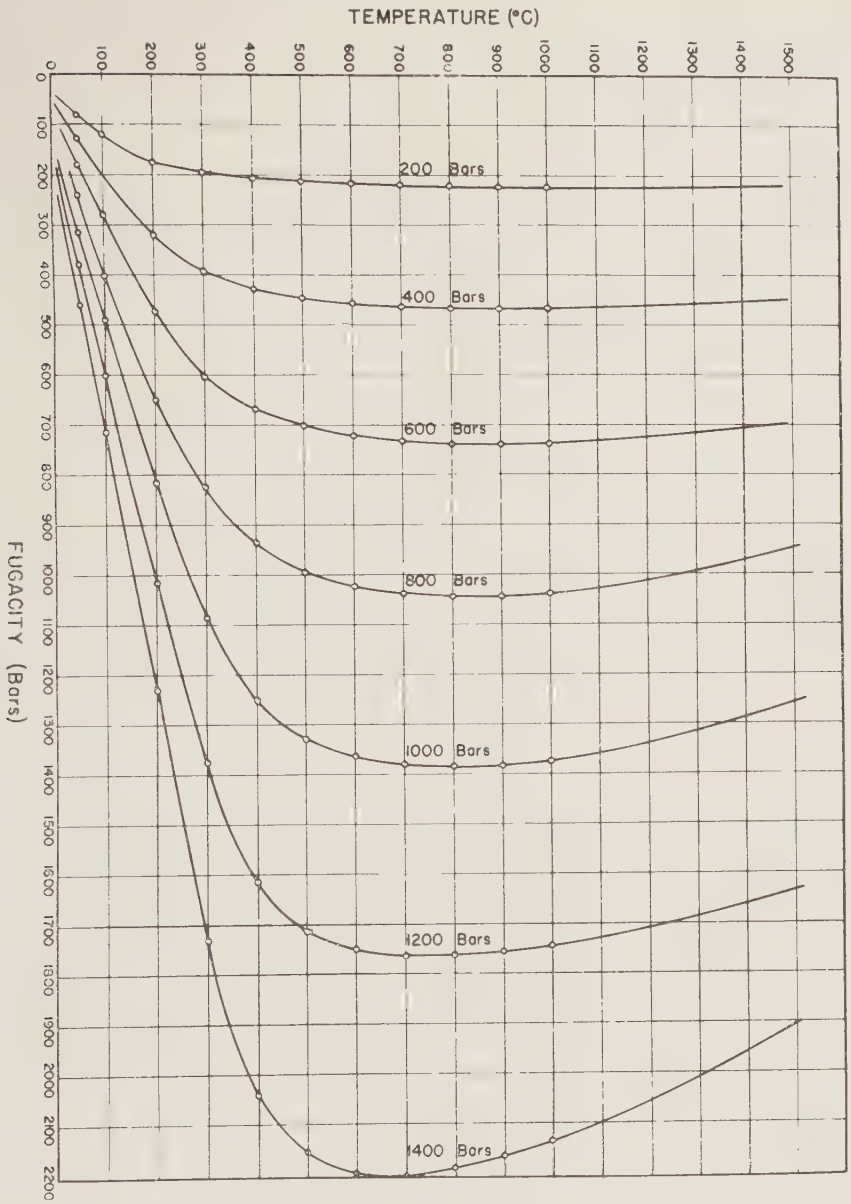


Fig. 1. (*a*)

Fig. 1. Plot of fugacity of CO_2 as a function of temperature and pressure.


TEMPERATURE (°C)
FUGACITY (Bars)
200 Bars
400 Bars
600 Bars
800 Bars
1000 Bars
1200 Bars
1400 Bars

(*b*)

In our case we have calculated the fugacities first and then obtained from them the free energies. The fugacities have been obtained from the relationship:

$$\ln p - \ln f = \frac{1}{RT}\int_0^P \alpha \, dp$$

where

$$\alpha = \frac{RT}{P} - v$$

The advantage of this method is well known and has been discussed by Klotz (1950). The α term is a difference term, and although the volume term itself

Table 1. Fugacity (f) values for CO_2 (in bars)

Pressure (bars)	Temperature in degrees centigrade										
	50°C	100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C	1000°C
25	23·08	23·87	24·75	25·17	25·4	25·53	25·64	25·73	25·8	25·85	25·
50	42·1	45·34	48·7	50·42	51·25	51·7	52·05	52·3	52·5	52·65	52·75
75	56·27	64·1	71·7	75·6	77·36	78·3	78·9	79·35	79·7	80	80·2
100	69·75	80·5	93·75	100·5	103·3	104·8	105·85	106·75	107·35	108	108·2
200	83	119·5	175·2	195·5	208·4	213·3	216·4	219·1	221	222·3	223·5
400	127·5	200·5	320	392	427·4	445	456	462·7	466	468·3	468·5
600	180·1	280	472	603	668·9	702·6	722·1	731·3	738·9	739	739
800	240	402·5	650	825	935	995	1025	1037·5	1042	1042	1039
1000	315	490	815	1085	1250	1330	1365	1380	1383	1381	1374
1200	380	600	1015	1375	1616	1713	1750	1763	1763	1755	1742
1400	460	715	1375	1730	2040	2153	2192	2200	2185	2160	2128

may tend to infinity, the difference term is more manageable. On a large-scale plot of this function vs. p, the curves may be smoothed and extrapolated to zero without involving very large errors. The integration was performed by counting of squares. The values obtained for the fugacities have been tabulated in Table 1 and are represented graphically in Fig. 1. It should be pointed out that the usual random errors are present in the data, and that these have been smoothed out in drawing the curves. However, in the high-temperature region, where the fugacities become nearly constant, there is a more noticeable scatter in the data.

Free-energy values were calculated from the fugacity data, using the equation:

$$F - F^0 = RT \ln f.$$

$F^0_{T°K}$ for CO_2 has been calculated from the relationship

$$F^0_{T°K} = (H^0_{T°K} - H^0_{0°K}) - T_{°K}S^0$$

The values for the function $(H^0_{T°K} - H^0_{0°K})$ are tabulated in Rossini's tables (1947), as are the entropies.

Recently, Price (1955) has also calculated enthalpies and entropies for CO_2 from these data. When the free energies were calculated from Price's results

Table 2. Free energies ($-F$) of CO_2 (cal/mole)

Temp. (°C)	Pressure in bars										
	25	50	75	100	200	400	600	800	1000	1200	1400
50	12,192	11,808	11,622	11,485	11,372	11,099	10,878	10,694	10,520	10,400	10,278
100	14.456	13,983	13,727	13,558	13,267	12,867	12,638	12,370	12,224	12,075	11,945
200	19,394	18,760	18,398	18,147	17,561	16,997	16,633	16,333	16,121	15,916	15,631
300	24,540	23,752	23,292	22,969	22,214	21,424	20,936	20,580	20,269	20,000	19,740
400	29,589	28,653	28,105	27,719	26,784	25,827	25,229	24,783	24,396	24,054	23,384
500	34,941	33,860	33,225	32,779	31,691	30,565	29,866	29,333	28,889	28,502	28,151
600	40,591	39,367	38,648	38,141	36,902	35,615	34,820	34,215	33,720	33,290	32,901
700	46,042	44,675	43,872	43,301	41,915	40,475	39,593	38,920	38,369	37,897	37,470
800	51,793	50,283	49,396	48,765	47,229	45,644	44,664	43,934	43,328	42,817	42,360
900	57,745	56,093	55,121	54,424	52,747	51,016	49,956	49,158	48,503	47,947	47,465
1000	63,796	62,003	60,945	60,192	58,363	56,497	55,348	54,490	53,785	53,187	52,682

at a series of points chosen at random, agreement was not worse than 3·5%. Our values tend to be systematically lower (less negative), and this may be due to the inaccuracy of $\int \alpha \, dp$ in the low-pressure region. We do not believe that the experimental data justify any greater degree of rigour in the calculations.

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Relation of minor-element content of serpentines to their geological origin*

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We have been studying the serpentine group of minerals since 1943, as time permitted, in connection with several mineralogical and petrological problems. A large number of single specimens from worldwide localities and suites from various occurrences in the United States have been examined. Most of our data have been obtained from a collection of twenty chemically analysed serpentines (Table 1), but only part of the data is given here. We have made many differential thermal analyses, dehydration studies, X-ray powder diffraction patterns, and spectrographic analyses. Some of the results and conclusions of this study are incorporated in a paper by Nagy and Faust (submitted to the editor of the *American Mineralogist*). The complete set of these data together with their correlation and interpretation will be published later by the U.S. Geological Survey.

The availability of this fine collection of analysed and selected materials offered an unusual opportunity to correlate the mineralogical and petrological data with the geochemistry of the specimens studied. This note presents the conclusions we have drawn from our research on the relation of minor elements to the kinds of rocks in which the serpentines are found.

The samples used in this study were all prepared by carefully crushing large fragments down to the size where the serpentine became unlocked from associated minerals. These grains were then handpicked under a binocular microscope or jeweller's loupe, and the purified samples crushed to a still finer size and re-examined. After the entire sample was crushed to pass through a 100-mesh-sieve, it was re-examined for impurities under the petrographic microscope. Almost all of the samples thus prepared contained no detectable impurities, but in a few samples small specks of chromite so finely divided as to preclude further purification were present. In only one specimen did the Cr_2O_3 amount to as much as 0·22%. If we assume that all of this Cr_2O_3 is present in chromite, and there are valid reasons to doubt this, then the maximum chromite content would have amounted to only 0·32%.

The name *serpentine* has various connotations. In this paper we use the word serpentine to refer to a member of the serpentine group of minerals. Ultrabasic rocks which contain a mineral (or minerals) of the serpentine group are here designated Class *A*, which includes dunites, pyroxenites, peridotites, and related rocks; the serpentine-bearing rocks of various types of metamorphic origins are designated Class *B*, which includes metamorphozed limestones and

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dolomites, contact metamorphic deposits, and hydrothermal veins. Our minor-element studies apparently do not differentiate between the serpentines of the two types of ultrabasic rocks within Class A, the alpine-type peridotites and the

Table 1. Localities of the specimens of serpentine group minerals studied

Sample No.	Class *A* (in ultrabasic rocks)	Sample No.	Class *B* (in metamorphosed limestones, dolomites, etc.)
F-1	State Line Pits, Lowes mine, approximately 1·2 miles west-northwest of Rock Springs, Cecil County, Maryland	F-8	Smithfield, Windsor County, Rhode Island
F-3	Near Forest Hill, Harford County, Maryland	F-13	Tilly Foster iron mine, near Brewster Station, Putnam County, New York
F-15	North of Domo d' Ossola in Val Antigorio, Novara Province, Piedmont Region, Italy	F-14	Pei-wa-ku and Lao-yeh-ling, Hsiu-yen Hsien, Liaoning Province, Manchuria
F-19	Bare Hills, Baltimore County, Maryland.	F-20	Asbestos deposits, Gila County, Arizona
F-40	Prairie Creek area of peridotite in T. 8° S., R. 25°/W., $2\frac{1}{2}$ miles south-southeast of Murfreesboro, Pike County, Arkansas	F-22	Turkey Hill, near Montville, Morris County, New Jersey
F-42	Near Norris, Tennessee	F-23	Dognácska, 10 km west from Reschitza, Hungary
F-43	Crump's Quarry, Mineral Hill, $\frac{1}{4}$ mile north of state road, about one mile west of Media, Middletown, Pennsylvania	F-24	Montville, Morris County, New Jersey
F-46	Near Bellows Falls, Windham County, Vermont	F-25	Montville, Morris County, New Jersey
F-47	Tyrol, Austria	F-41	Windous deposit, Currant Creek magnesite deposits, White Pine County, Nevada
		F-53	Asbestos deposits, Grand Canyon, Arizona (presumably from the same general area as F-20)
		F-56	Fifth level, at the shaft, Gouverneur Talc Company, Balmat, New York

alnoite, kimberlite, mica-peridotite suite (see Hess, 1955). Specimens F-40 and F-42, Table 1, belong to the later suite.

The process of serpentinization is usually defined as the formation of serpentine from pre-existing ferromagnesian or magnesian minerals by hydrothermal solutions.

Chlorite, talc, stevensite, saponite, and other hydrous magnesian silicates commonly occur with serpentine.

The specimens selected for the spectrographic study of the minor elements were those for which we have chemical analyses. Other spectrographic data on serpentines in our files were also considered in drawing our conclusions. We have divided the serpentine minerals into the two classes, previously mentioned, based on their origin. Class *A* contains nine specimens from localities where ultrabasic rocks crop out. These serpentines were formed by deuteric or subsequent hydrothermal alteration of the original ultrabasic rocks. Class *B* contains eleven

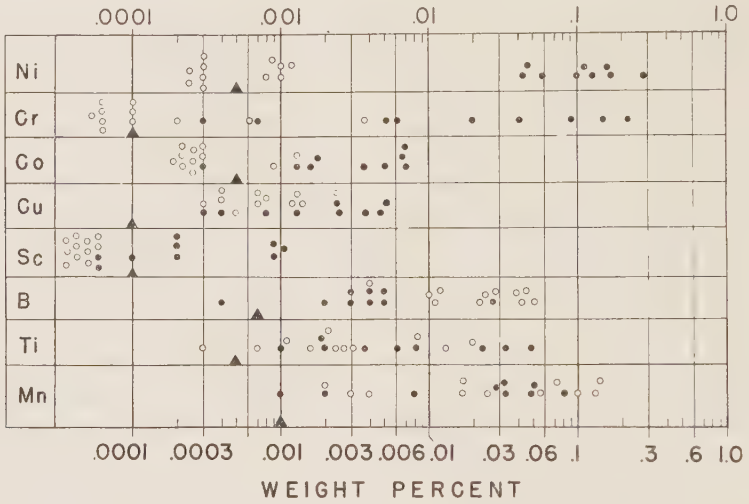

Fig. 1. Graphical representation of the concentration of some minor elements in the serpentine group minerals. Triangular black index represents sensitivity limit for the element. Points to the left of the index are samples in which the element was not detected. Solid circles represent serpentines associated with ultrabasic rocks. Empty circles represent serpentines from other rock associations.

specimens found chiefly in metamorphozed limestones and dolomites, in contact metamorphic deposits, and in hydrothermal veins. Except for the vein deposits, the serpentines have been formed by hydrothermal replacement of pre-existing ferromagnesian or magnesian minerals.

Spectrographic analyses were made for the following chemical elements: Ni, Cr, Co, Sc, Cu, B, Mn, Ti, Zr, Al, Ca, Ba, Zn, Ge, Ga, As, V, Na, and Be. In addition, mercury was determined for four serpentines of Class *A* and four of Class *B*. The following elements were not found: Ag, Au, Cd, In, Tl, Sn, Pb, Bi, Te, Pt, Mo, W, Nb, Y, Sb, La, Li, and P.

The data for eight elements in our study are given in Fig. 1.

The minor elements of serpentines are of unusual interest, because they were in part inherited from the parent rock that was serpentinized and in part introduced from external sources. Their study, therefore, provides valuable information regarding the chemistry of the serpentinization process.

In general, ultrabasic rocks, which are the parent rocks for Class *A* serpentines, are considerably richer in minor elements than magnesian limestones, which are the

parent rocks for many of the Class *B* serpentines. This difference in the composition of the parent rocks is retained more or less intact in the serpentines and explains the generally higher percentages of nickel, chromium, cobalt, and scandium in serpentines of Class *A*. The minor-element composition of the parent rocks of the samples studied is not known; hence, it is necessary to base the present discussion on (1) published, average compositions of such rocks and (2) mineralogical data and paragenetic studies. Some of the data in the literature on minor elements in ultrabasic rocks are based on samples that were serpentinized, but it has not been practical to eliminate such data and recompute the average abundances of the various elements. For a more precise examination of the chemistry of serpentinization, both the parent rocks and related serpentines need to be studied together.

There is a distinct difference in the concentration of nickel between the two classes of serpentines. No serpentine of Class *A* contains less than 0·04% Ni, whereas no serpentine of Class *B* contains more than 0·002% Ni. A whole order of magnitude of concentration separates the two classes, and an intermediate value, say 0·01%, might be used as the bounding value. If a serpentine of unknown classification were analysed for nickel and found to contain 0·01% or more, the present data indicate that it belongs in Class *A*.

According to Wells (1943) and Goldschmidt (1954, p. 670), the nickel content of ultrabasic rocks ranges from 0·01 to 0·4%, and that of calcareous and dolomitic rocks is a few parts per million or less. As these ranges correspond well with the ranges in the two classes of serpentine, it seems safe to conclude that nickel is neither lost nor introduced in the process of serpentization. It should also be noted that nickel occurs to a lesser extent in nickeloan stevensite, pimelite, talc, and chlorite; these minerals are commonly associated with serpentine minerals.

Chromium, like nickel, is known to be high in ultrabasic rocks, and correspondingly, Class *A* serpentines tend to be higher in this element than those of Class *B*. The range of concentration is, however, much greater than for nickel, and there are two samples of Class *A* serpentines that contain only a few parts per million of chromium. Unlike nickel, which is an integral component of olivine and other major silicate minerals of ultrabasic rocks, chromium is present in the form of the accessory mineral chromite, which may be distributed very erratically in these rocks. Hence the chromium content of an ultrabasic rock could vary greatly from one hand specimen to the next, even from a single body of rock, depending on the amount of chromite that happened to be present in each specimen. The large variation in the chromium content of Class *A* serpentines is, therefore, ascribed to this erratic distribution of chromite in the parent rock rather than to any movement of chromium in or out of the rock during serpentinization. Examples of kämmerite forming through the alteration of chromite have been described (Miller, 1953), but the close association of the two minerals indicates that chromium does not move any great distance during this reaction. The presence of 0·01% or more of chromium is indicative of Class *A* serpentine.

Cobalt ranges from 0·001 to 0·007% in Class *A* serpentines, except for sample F-40, which it is abnormally low. Among Class *B* serpentines, it is below the limit of detection (0·0005% Co) in nine out of eleven samples and about 0·001% in two samples.

Scandium is known to substitute for magnesium in minerals of the ultrabasic rocks but its content in dolomites and magnesian calcite is extremely low (Rankama and Sahama, 1950 pp. 516–517). The element was detected only in Class *A* serpentines.

Copper, titanium, and manganese concentrations in the serpentines are non-diagnostic for determining the genetic class to which a serpentine belongs.

Boron is present in the serpentines, and ranges from 0·0003 to 0·015%. The data suggest that Class *B* serpentines tend to be richer in this element. Sahama (1945) studied the boron content of ultrabasic rocks from Finland and found concentrations in the range of 0·003 to 0·03% boron. He correlated the boron content with the degree of serpentinization of the dunites and concluded that boron was introduced during the serpentinization process. Other observations, such as those of Duparc and Sigg (1914) on the presence of tourmaline in serpentine-bearing rocks, have also suggested that boron might be associated with ultrabasic rocks. Our studies are not directly comparable with those of Sahama, for we did not study the relation of the fresh ultrabasic rocks to altered rocks containing successive increments of serpentine. The question of the relation of boron in the serpentines of Classes *A* and *B* to the parent rock is complicated by the occurrence of pegmatites at many localities. The trend for the Class *B* serpentines to be richer in boron seems to be a true one.

In summary, we have found that the study of the minor elements in serpentines is of diagnostic value in studies on mineral genesis. Class *A* serpentines may be easily differentiated from Class *B* serpentines by their concentrations of nickel in excess of 0·01%. Serpentines of Class *A* also tend to be significantly richer in chromium, cobalt, and scandium. Class *B* serpentines are richer in boron. In general, the concentrations of the minor elements in serpentines seem merely to reflect the concentrations of their parent rocks. Boron appears to be introduced from external sources. In some rocks, the boron may have been introduced by the fluids which formed the pegmatites associated with the serpentines.

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GEOCHEMICAL NOTES

Germanium in meteorites

(*Received* 19 *April* 1956)

EIGHT chondrites (including two composites) and seven meteorites were analysed for germanium. The meteorites analysed and their germanium content are recorded in the following table.

Meteorite	Ge (p.p.m.)		Meteorite	Ge (p.p.m.)
Chondrites			Irons‡	
Composite I (7 chondrites)*	10·3	10·9	Tlacotepec	<1·0
Composite II (7 chondrites)†	9·4	9·6	Duchesne	<1·0
Cope, Colo.	9·2	9·0	Toluca	271
Melrose, N. Mex.	9·3	9·6	Henbury	273
Arriba, Colo.	9·2	9·0	Edmonton	38
Ladder Creek, Kan.	6·6		Magura	519
Plainview, Texas	12·0		Cañon Diablo	352
Roy, N. Mex.	8·8			

Meteoritic material was put into complete solution by treatment with hydrofluoric acid followed by fusion of the residue with potassium pyrosulphate. Germanium is first separated by distilling the $GeCl_4$ from constant boiling HCl and then determined by measuring the absorbance of its phenylfluorone complex.

If, following UREY (*The Planets*, 1952, Yale University Press), we take chondrites to represent average cosmic matter (excluding the volatile elements) the present analyses give 9 p.p.m. for the cosmic abundance of germanium. Previous data on the meteoritic abundance of germanium (V. M. GOLDSCHMIDT, *Geochemistry*, 1954, p. 380) are probably too high.

Chondrites appear to be uniform in their germanium content and it seems probable that the average value of 9 p.p.m. for the cosmic abundance of Ge is not far from the truth. Present data (see table) for Ge in chondrites and in iron meteorites indicate that the distribution of Ge in meteorites is determined by conditions under which meteorites were formed. The difference in the range of Ge in iron meteorites and in the iron phase of chondrites may have an important bearing on the origin of meteorites.§ This work is

* Arriba, Colo.; Beenham, N. Mex.; Cope, Colo.; Coterfield, Neb.; Morland, N. Mex.; Plainview, Texas; Roy, N. Mex.

† Alamogordo, N. Mex.; Estacado, Texas; Gladstone, N. Mex.; Kingfisher, Okla.; Gruver, Texas; Ladder Creek, Kan.; Melrose, N. Mex.

‡ Because of very limited samples, error may be ±10%.

§ Preliminary fractionation of chondrites into the silicate and metal phases indicates that Ge is concentrated in the latter phase.

part of a study of the geochemistry of Ge which the author hopes to publish in the future.

I am indebted to Dr. E. B. Sandell, who provided the chondritic material, and Mr. W. Nichiporuk for placing the irons at my disposal.

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The association of nickel with cinnabar

(*Received* 28 *July* 1956)

In a preliminary study on geochemical associations with particular reference to sulphide minerals, one of the marked associations noted was that of nickel with cinnabar.

Table 1 shows results of the qualitative spectrochemical analysis for nickel in cinnabar specimens from the Oxford University Mineral Collection. In addition to this data

Table 1. Qualitative spectrochemical analysis of nickel in cinnabar specimens using the cathode-layer carbon arc

Specimen No.	Locality	Ni
5054	Stahlberg, Palatinate, Bavaria, Germany	x
18548	Bavarian Palatinate, Germany	x
483	Almaden, Spain	x
5060	Almaden, Spain	x
5059	Almaden, Spain	x
15451	Almaden, Spain	x
5063	Idria, Gorizia, Italy	x
479	Idria, Gorizia, Italy	
19875	New Almaden, California, U.S.A.	x
19876	New Almaden, California, U.S.A.	x
21519	Sinaloa, Mexico	
11315	Coquimbo, Chile	
11318	Borneo	

x = Nickel detected.
Probable sensitivity of detection c. 0·0002% Ni.

Ahrens (1956) has detected nickel in cinnabar specimens from various South African localities by spectrochemical analysis, while Dreyer (1940) has noted that some of the Californian quicksilver deposits contain small amounts of millerite, NiS. Ross (1942) has also reported the presence of millerite and other nickel minerals in minor quantities in certain cinnabar lodes.

Few other trace elements could be detected spectrochemically in the specimens listed in Table 1. Traces of iron were present in some specimens and most other elements identified were lithophile elements, such as silicon, strontium, barium, and aluminium, which were

probably present in minute amounts of extraneous minerals not completely removed in the preparation of the cinnabar samples for analysis.

Although only qualitative data appear to be available, the fact that nickel is associated with cinnabar from various localities may be of interest from the point of view of ore genesis. Although differences in environment give rise to differences in mineralogy and form of cinnabar deposits, the fundamental genetic features of all cinnabar lodes are believed to have much in common (e.g. see Ross, 1941, 1942). Cinnabar is almost always a primary mineral, which is thought to be deposited from ascending alkaline solutions or as a result of solfataric action. Nickel sulphide, like mercuric sulphide, is readily soluble in sodium-sulphide solutions, although in the case of NiS the solutions obtained are probably essentially colloidal. Hence if the nickel found associated with cinnabar specimens is present either as a trace constituent in the cinnabar crystal lattice or as the sulphide, the association is in agreement with one of the possible physicochemical mechanisms discussed by Krauskopf (1951), namely that cinnabar is transported to its point of deposition by alkaline sulphide hydrothermal solutions. Vapour-phase transport of the mercury forming cinnabar deposits, either as the metal, sulphide, or chloride, cannot account for the association of nickel with the mineral, since the volatilities of mercury, mercuric sulphide, and mercuric chloride are very decidedly higher than those of the corresponding nickel species.

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Book review

ALEXANDRE DAUVILLIER: **Cosmologie et Chimie**. Presses Universities de France, 108, Boulevard Saint-Germain, Paris, 1955. viii + 217 pp. 900 fr.

THE author has set out to describe the origin of the chemical elements and the evolution of the universe on the basis of the most recent scientific results. In the first chapter he discusses the occurrence of the chemical elements in the sun and in the stars, in interstellar matter, in meteorites, comets and planets, and, finally in cosmic radiation. In the further chapters an attempt is made to draw theoretical conclusions from the facts available. The author infers that "there is a statistic equilibrium between materializations and dematerializations owing to the combined interplay of high temperatures and electromagnetism." This view he presents as "no longer in doubt."

It is obvious that a survey including such varied topics as astronomy, spectroscopy, and radioactivity (in the widest meaning of the term) cannot show equal expertise in all details; e.g. the extensive reproduction (p. 78) of a completely worthless paper about the radioactivity of meteorites, whose gross mistakes were pointed out immediately after its publication, might with advantage have been left out; the biggest iron meteorite, still lying in South Africa on the spot where it fell, is erroneously transferred (p. 70) to the New York Museum.

Not the least attractive aspect of the book is the discussion of a great number of older observations and theories, amply illustrated by quotations. It is all the more to be regretted that the variegated and rich contents of the book are not made more easily accessible by an index; the "Table des Matières" at the end of the book comprises only twelve lines. To dispense thus with a proper register is a French habit which to most scientists would seem a custom more honoured in the breach than the observance, and it is to be hoped that in a future edition the author will take the wishes of such readers into account.

F. A. PANETH

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and should include the standard abbreviated title of the journal, year, volume number, and page number.

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It is in those branches of natural science which border older established disciplines that the need for critical survey reviews of progress has become greatest. This has arisen partly because subjects such as geochemistry and geophysics fringe and overlap so many other fields and partly because they are at present vigorous growing points in science. A principal aim of the annual series, Chemistry and Physics of the Earth, will be to provide authoritative and up-to-date surveys of progress for those actively engaged in geophysics and geochemistry. But it is hoped also that much of what is written will encourage the interest of the chemist and physicist in a study of our planet, not merely for its own sake, but because such a study often turns out to be of benefit to physics and chemistry. Another aim is to acquaint the geologist with the results and methods of geophysics and geochemistry, particularly as progress in earth science has been hindered by some lack of liaison between different groups. An attempt will be made to provide a balanced variety of topics with roughly equal emphasis on chemistry and physics, but certain topics will be considered fairly regularly.

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